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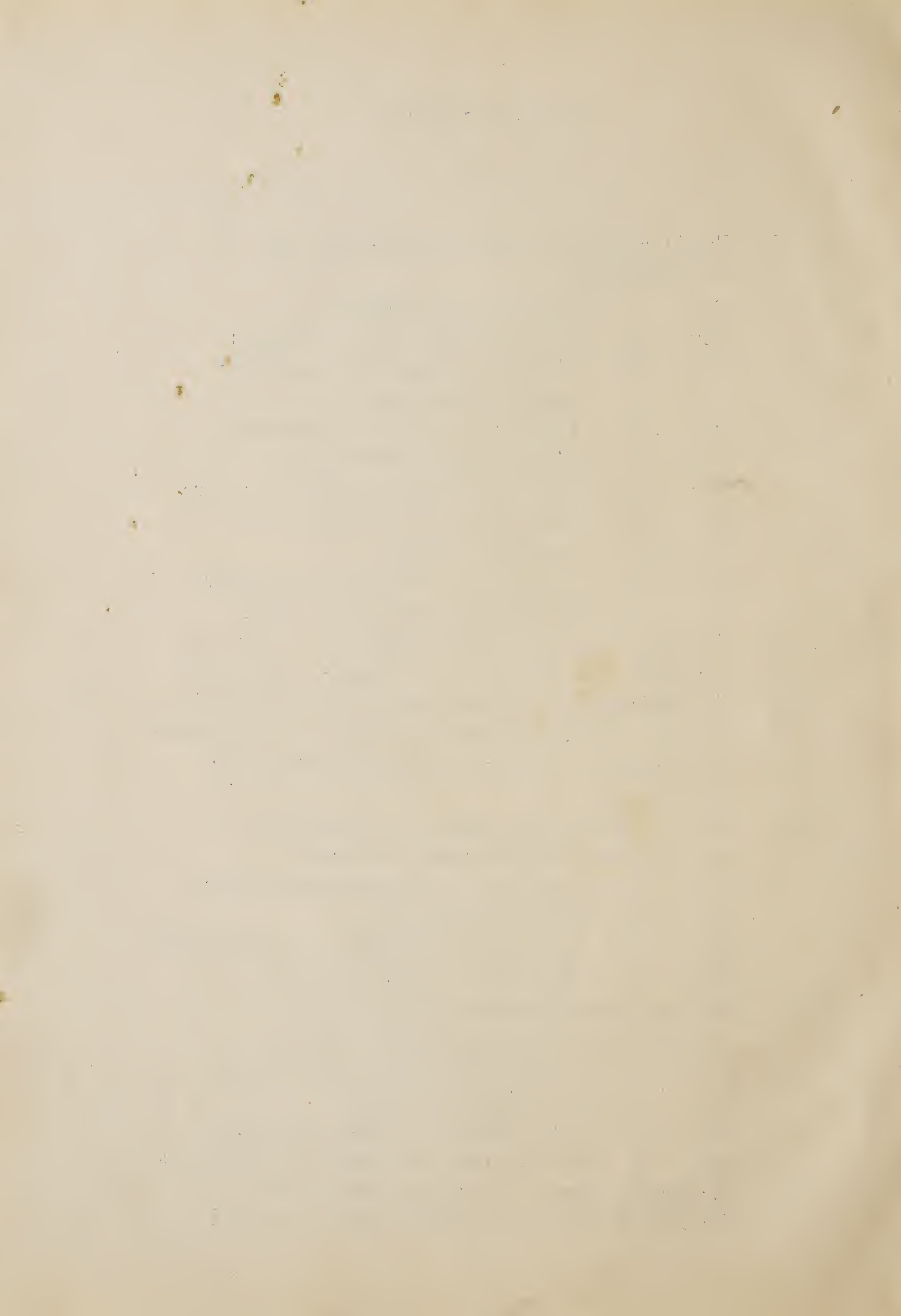
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# THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE

## Part I. Materials and Methods

BY SIR C. V. RAMAN

(Memoir No. 129 of the Raman Research Institute, Bangalore-6)

Received November 11, 1961

### 1. INTRODUCTION

DIAMOND is a material of extraordinary interest and importance. Both by reason of the simplicity of its structure and composition and by reason of the variety of techniques available for the investigation of its spectroscopic behaviour, the study of diamond offers a most promising approach to the elucidation of the fundamental aspects of crystal physics. Questions such as the following need an answer. What is the nature of the atomic vibration spectrum of a crystalline solid and how is it related to its structure? Why does the passage of light through a crystal result in its diffusion with a change of frequency? In what circumstances and in what manner does the absorption of infra-red radiation occur in its passage through a crystal? How are the spectroscopic properties of a crystal related to its thermal energy content? Answers to these and many other questions are furnished by the facts which emerge from a study of the spectroscopic behaviour of diamond.

A remarkable property of diamond is that even selected material of the highest quality shows an astonishing variation of behaviour in certain respects, including especially its transparency to ultra-violet light and to infra-red radiation. Specially noteworthy also are the enormous variations observed in the intensity and spectral character of the visible luminescence exhibited by diamond under ultra-violet illumination. The explanation of these and other variations and the correlations which exist between them is an important part of the field of research presented by diamond and adds greatly to the interest of the subject. But in recognising this, one should not overlook the importance of finding answers to the fundamental questions which arise in respect of all diamonds. Indeed, not unless the more general questions have been satisfactorily answered can we hope to give the correct replies to the question why particular diamonds differ amongst themselves.

The morphology, structure and properties of diamond have interested the writer and have been the subject of numerous investigations and published



reports by him and his collaborators in earlier years. To enable these studies to be undertaken, specimens were acquired from time to time and the collection thus built up now includes some hundreds of diamonds of varied origins and of diverse forms and qualities. Crystals of diamond in their natural forms as found near Panna in Central India and from the South African mines form the most attractive items in the collection. But by far the most useful specimens included in the collection are the flat polished plates, one hundred in number, which are of diverse thicknesses and sizes and exhibit varied types of behaviour. There is no more convenient form of diamond for examining its optical properties than a flat polished plate, especially if its faces have a known crystallographic orientation, as is frequently the case for the plates in the writer's collection. It is obvious that for a real understanding of the problems presented by diamond, it is necessary to study such an extensive range of material and to examine the individual diamonds in detail in respect of diverse properties, and then to compare and correlate the results thus obtained. One of the most surprising facts about diamond is the existence of the correlations which come into evidence in an extremely striking and convincing fashion in such studies. That they must be recognised and need to be explained is obvious. But more important still is the fact that they point the way to a real understanding of the nature and properties of diamond.

## 2. METHODS OF STUDY

It had long been the desire of the writer personally to study the infra-red behaviour of the entire collection of plates of diamond in his collection. But only recently however has the acquisition for this Institute of a Leitz recording infra-red spectrophotometer provided with both NaCl and KBr optics enabled this project to be seriously undertaken. The region of wavelengths between  $1\mu$  and  $15\mu$  can be traversed with the NaCl optics and between  $13\mu$  and  $24\mu$  with the KBr optics. With the spectrograph properly adjusted and worked, it becomes almost a routine operation to record the percentage transmission curves in these ranges. A special point of importance which has to be attended to is the most appropriate speed of operation. To get out the records quickly, one might be tempted to tend to run the spectrograph at the maximum permissible speed. But experience shows that, especially with the plates of smaller area, this is an erroneous procedure to follow. The best records are those in which the recording apparatus is set at slow speed as the maximum of detail and the highest definition are then obtained. Merely to record the percentage transmission curves of a large number of plates can serve no useful purpose unless one also examines each individual plate by other methods of study which can throw some light



on the nature of the material under investigation. Of such methods there are several. But we shall here mention only three techniques which involve the minimum of labour and at the same time are highly revealing. The first is the examination of the transparency of the material in the ultra-violet region of the spectrum. The second is the absence or presence of birefringence. The third is the visible luminescence of the diamond under ultra-violet illumination and especially the variations of the intensity and the colour of such luminescence.

A simple method of examination for ultra-violet transparency is to place the plate of diamond on a sheet of uranium-tinted glass which fluoresces strongly under ultra-violet illumination. A convenient source of such illumination is that commonly used for examining the luminescence of minerals, *viz.*, a mercury vapour lamp in a tube of fused quartz, enclosed in a metal case one side of which is open but is covered by a filter which cuts off the visible light but allows the ultra-violet radiation of the lamp to pass through. When the lamp is held over the diamond, its transparency or lack of transparency is immediately revealed by the appearance presented by the glass plate as viewed either from above or from below. The area covered by the diamond appears dark if it is opaque and bright if it is transparent. While this simple technique suffices for a qualitative examination of the ultra-violet transparency of diamond, it is desirable to use the  $\lambda$  2536.5 resonance radiation of the mercury arc isolated by a quartz monochromator for more critical studies in which it is sought to observe and photograph the variations, if any, which the plate of diamond exhibits in respect of its ultra-violet transparency over its entire area. We shall in a later part of this memoir return to the results obtained in this manner.

Examination of a diamond plate for the presence or absence of birefringence is a very simple matter. The diamond is placed on a strain-free glass plate and viewed through a pair of crossed polaroid sheets against a brilliant source of white light. Even the faintest birefringence becomes visible in these circumstances. The nature and character of the birefringence, if any, that is present can be determined by examination through a magnifier of appropriately chosen power.

The technique for observing the luminescence of the diamond is equally simple. The plate of diamond is placed on a sheet of black glass and a beam of sunlight filtered through a sheet of black glass which transmits only the ultra-violet part of the solar spectrum is focussed on it. The presence or absence of luminescence and its colour and intensity, if present, then become evident to observation. The use of filtered sunlight in the experiment ensures

that the illumination of the diamond is of adequate intensity, so that a feeble luminescence is not mistakenly regarded as indicating the absence of luminescence. It is by no means generally the case that luminescence when present has the same intensity or colour over the entire area of the plate. It is possible, of course, to record the luminescence patterns of the diamond in such cases photographically on a colour film. It is sufficient, however, to photograph the luminescent diamond on ordinary film through appropriately chosen colour filters so as to exhibit these variations. We shall return in a later part of the memoir to this aspect of the subject.

### 3. SUMMARY

The author's collection of diamonds includes one hundred polished plates of diverse thicknesses and sizes and exhibiting a varied behaviour. This form of diamond is exceptionally well suited for critical studies of the optical properties of diamond. The importance in the study and interpretation of the infra-red absorption by diamond of a parallel investigation of other properties is indicated. Of particular importance are three of them, viz., ultra-violet transparency, birefringence and luminescence. Simple and convenient methods for studying them are described.



# THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE

## Part II. A General Survey of the Results

BY SIR C. V. RAMAN

*(Memoir No. 129 of the Raman Research Institute, Bangalore-6)*

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### 1. INTRODUCTION

WE now proceed to indicate in broad outline the results which have emerged from the investigations envisaged in the first part of this memoir. The outstanding facts of the subject will be stated and illustrated in an appropriate manner.

A critical examination of the optical behaviour of all the one hundred polished plates of diamond in the writer's collection reveals that they fall into three groups. Two groups of diamonds which we shall designate here as group A and group B each form about ten per cent. of the entire number of specimens. The remaining eighty per cent. of the diamonds will here be designated as group C. The diamonds in group A exhibit certain physical properties which are common to all of them and which distinguish them from all the other diamonds in the collection. The diamonds in group B also exhibit certain physical properties which are common to all of them and which distinguish them from all the other diamonds in the collection. But the properties of the diamond in group A and the properties of the diamond in group B are so strikingly contrasted that the observer is obliged to infer that they represent fundamentally different forms of diamond. That this is actually the case and that the crystal structures of the diamonds in group A and group B are indeed dissimilar, is demonstrated by the characters exhibited by the infra-red absorption spectra of the two groups of diamond. Their spectral behaviours are completely identical in some respects and completely dissimilar in other respects. Considered in conjunction with the other differences alluded to, it is clear that the facts admit of no explanation other than that we are here concerned with basic differences in crystal architecture. What these differences are is indicated in an unmistakable fashion by the spectroscopic observations.

The remaining eighty per cent. of the diamonds which we have classed together as group C are shown by the studies to be *composite diamonds*, in other words, diamonds in which the structures characteristic of group A and the structures characteristic of group B are present side by side in the same specimen in juxtaposition. This is not an inference from theory but is a statement of actual facts of observation. The geometric patterns of various sorts which these composite diamonds exhibit are visual evidences that over the area of any one cleavage plate of diamond, there are some parts which exhibit the characteristic properties of the diamonds of group A while the other parts exhibit the characteristic properties of diamonds of group B. Moreover, these parts are distributed over the area in regular crystallographic patterns which by themselves conclusively demonstrate that the diamonds of group A and the diamonds of group B are distinct crystallographic entities different from each other.

## 2. THE PHYSICAL BEHAVIOUR OF GROUP A AND GROUP B DIAMONDS

Ten diamonds of group A in the writer's collection and eight diamonds of group B have been set side by side and examined under identical conditions. The photographs of the two groups of diamond reproduced and exhibited alongside of each other in Plate I were recorded simultaneously and with identical exposures and hence are strictly comparable with each other. The infra-red transmission curves of the largest diamond in group A and of the largest diamond in group B were also recorded in the NaCl range of the Leitz infra-red recording spectrophotometer and are reproduced respectively as Fig. 1 and Fig. 2 in the text below.

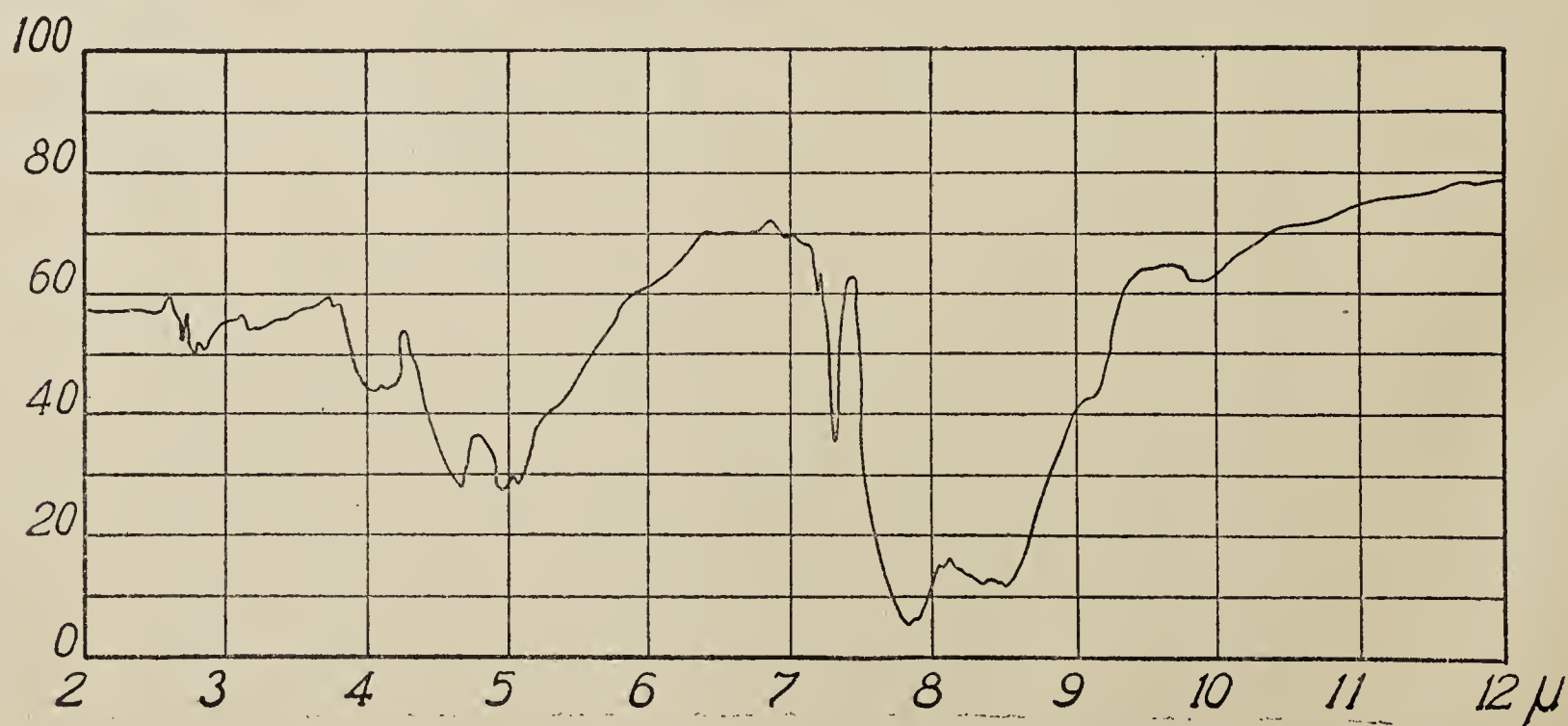


FIG. 1. Infra-Red Transmission of Group A Diamond (Thickness 1.01 millimetre).



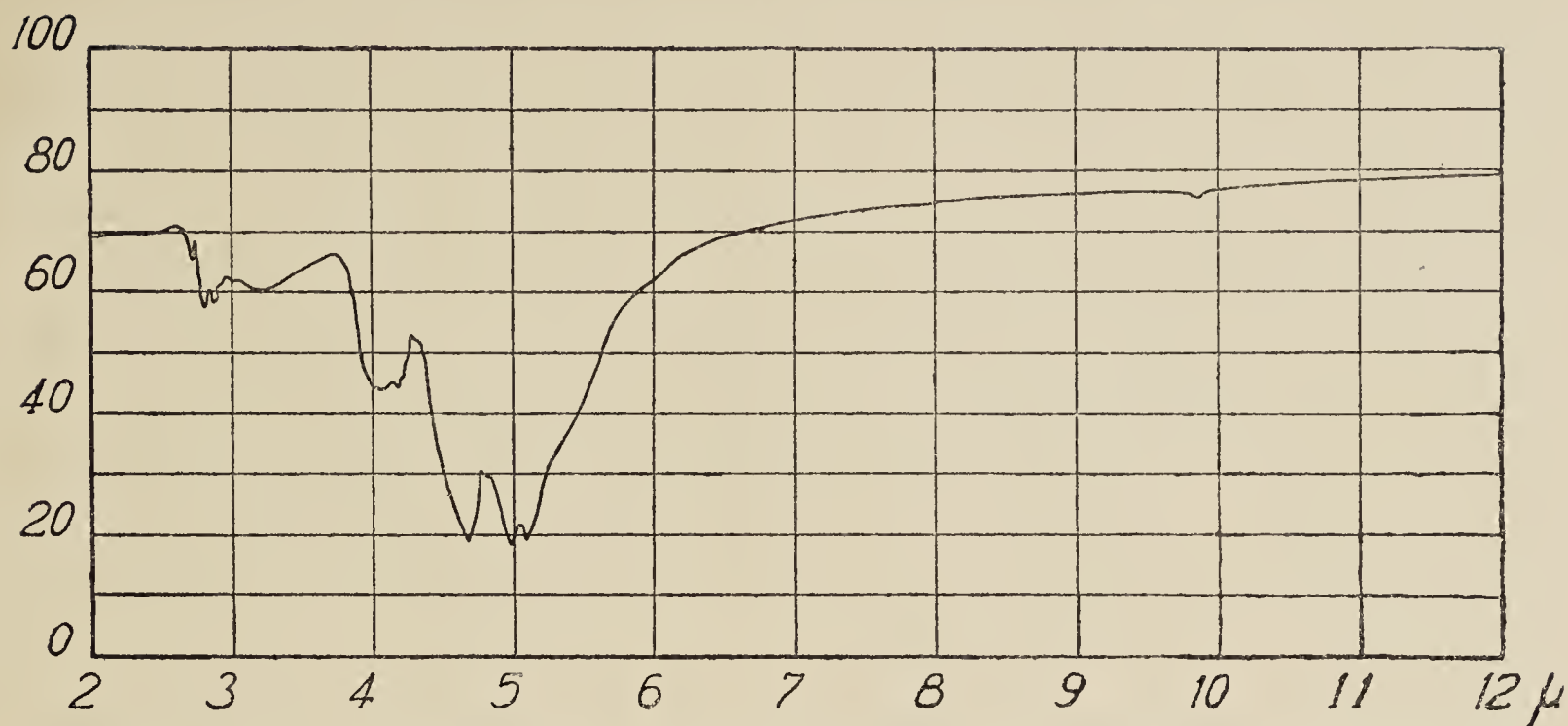


FIG. 2. Infra-Red Transmission of Group B Diamond (Thickness 1.06 millimetre).

Turning to the photographs reproduced in Plate I, we remark that the two pictures marked (a) and (a) respectively on its left and right sides exhibit the appearance of diamonds belonging respectively to the two groups as viewed between crossed polaroids against a bright white source of light. While the edges of the ten diamonds of group A are visible by reason of the light refracted at their peripheries, the plates themselves appear quite dark. In other words, the diamonds of group A are non-birefringent, and may hence be described as *truly isotropic and optically perfect diamonds*. On the other hand, all the eight diamonds of group B exhibit a marked restoration of light as seen between crossed polaroids. The patterns of birefringence which they exhibit differ from diamond to diamond both in respect of intensity and their geometric configuration, but in none of the eight specimens is the birefringence absent. Thus, we are justified in stating that the exhibition of a visible birefringence is a general characteristic of the diamonds of group B. We shall revert later to a more detailed consideration of the specific features of such birefringence.

The same ten diamonds of group A and eight diamonds of group B were examined for their transparency in the near ultra-violet region of the spectrum by the methods already described and explained in the first part of this memoir. They were placed on sheets of uranium-tinted glass and their transparency or opacity (as the case may be) in the near ultra-violet region of the spectrum stands immediately revealed by the luminosity of those sheets, as is seen from the photographs reproduced in Plate I and marked (b) and (b) respectively on the left and right of the pictures. It will be seen that all the diamonds of group A exhibit complete opacity, while those of group B are highly transparent to the part of the spectrum under consideration. As between them-



selves, the eight diamonds of group B exhibit some differences in respect of their transparency. These differences are ascribable to a slight yellowish tinge exhibited by some of the specimens, while the others are perfectly colourless.

Finally, the photographs reproduced in Plate I and marked (c) and (c) respectively on the left and the right exhibit the behaviour of the same ten diamonds of group A and the same eight diamonds of group B in respect of the luminescence excited by the incidence of ultra-violet radiation. The two groups of diamond were placed side by side on a sheet of ordinary glass and strongly illuminated by the light of three mercury lamps enclosed in Wood's glass which cut out all the visible light except some deep red. The glass sheet with the diamonds adherent to it was photographed through a cell containing an aqueous solution of sodium nitrite. This filter cuts off the scattered or reflected ultra-violet light and allows only the visible luminescence to come through. It will be seen from the Plate that all the diamonds of group A exhibit a visible luminescence but with very different intensities in the different diamonds. The colour of the luminescence as actually observed was a clear blue in all cases. On the other hand, all the diamonds of group B are seen to be definitely non-luminescent.

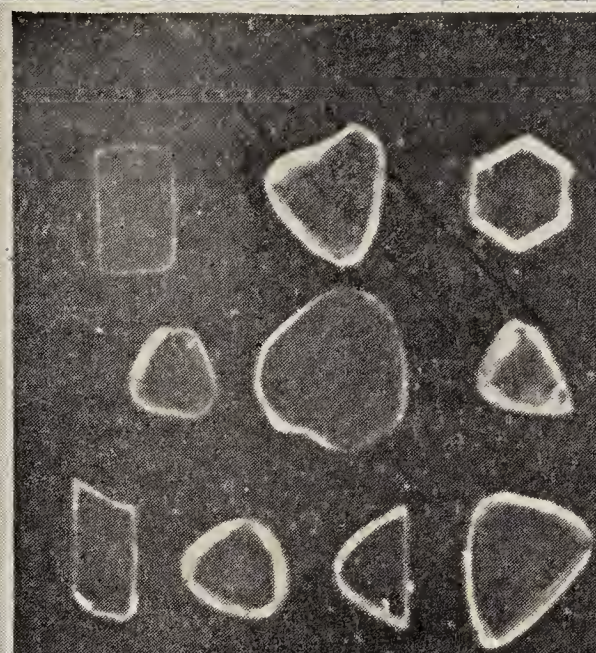
We may sum up the information exhibited by Plate I as follows: The diamonds of group A are isotropic and optically perfect diamonds. They are opaque to ultra-violet radiation less than  $0.3\mu$  in wavelength, and exhibit a visible blue luminescence under ultra-violet irradiation but of varying degrees of intensity. On the other hand, the diamonds of group B exhibit a readily observable birefringence, are transparent to ultra-violet radiation of wavelengths between  $0.3\mu$  and  $0.25\mu$ , and are non-luminescent. These properties of the two groups of diamond go hand in hand with the differences in the behaviour towards infra-red radiation exhibited in Figs. 1 and 2 in the text above. A detailed discussion of the features noticed in these spectrographic records will appear in later parts of this memoir. It will suffice here to draw attention to some of their outstanding features. The thickness of the group B diamond whose record is reproduced in Fig. 2 is distinctly greater than that of the group A diamond whose record is reproduced in Fig. 1. Due allowance being made for the effect of the greater thickness on the percentage transmission curves, it will be seen that in the spectral region between  $2\mu$  and  $6\mu$ , the two diamonds exhibit features which are indistinguishable from each other. On the other hand between  $6\mu$  and  $12\mu$ , the behaviour of the two diamonds is totally dissimilar. The group A diamond exhibits an absorption which goes up steeply beyond  $7\mu$  and a whole series of absorption maxima



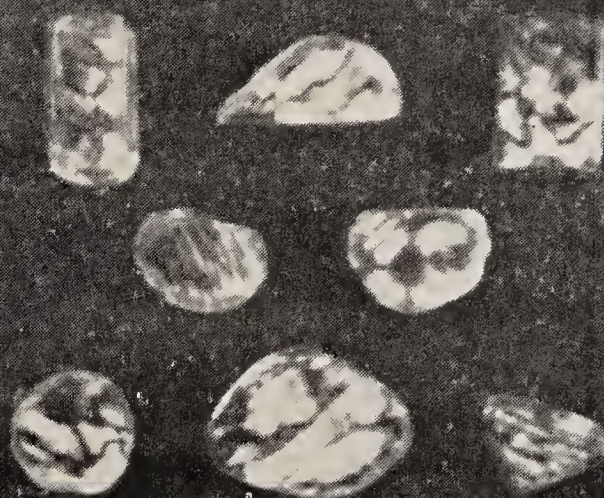
Group A

Group B

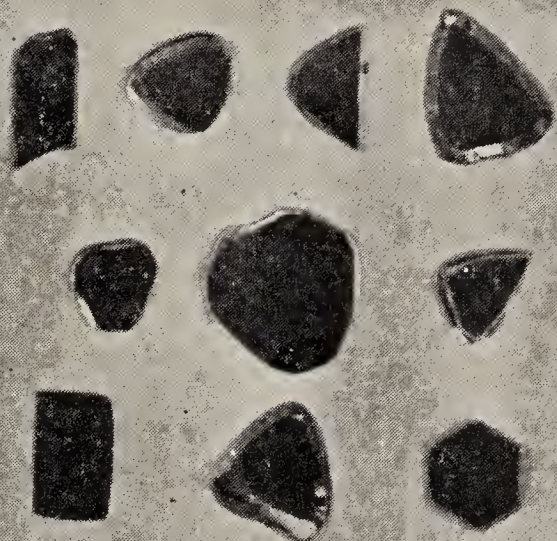
(a)



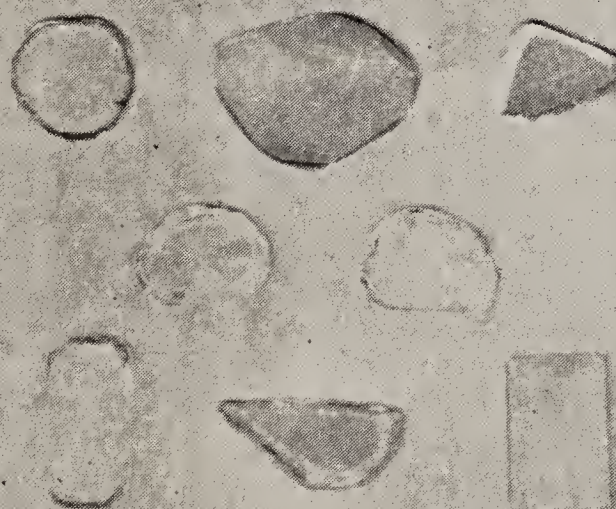
(a)



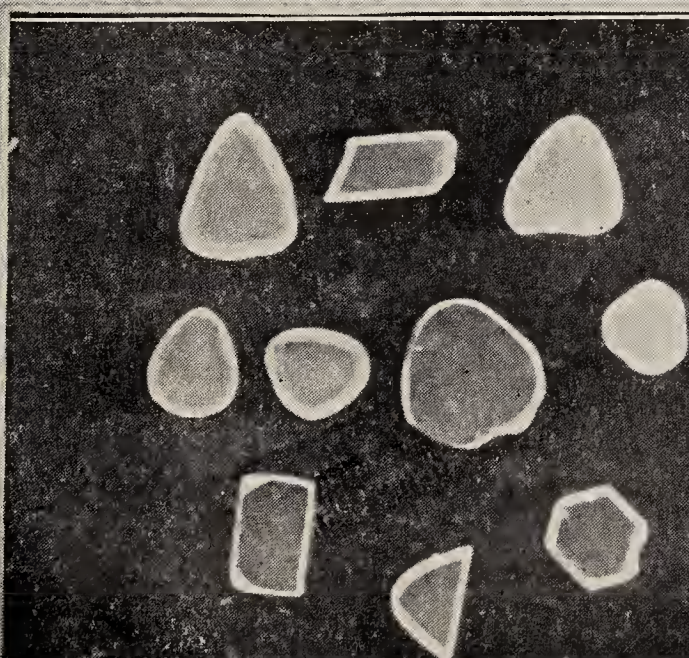
(b)



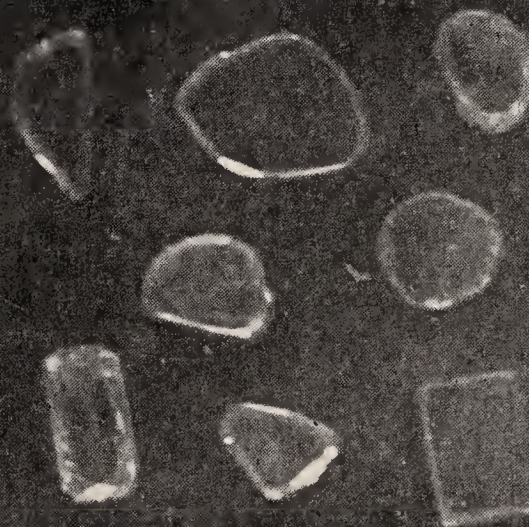
(b)



(c)



(c)



Ten diamonds of Group A and eight of Group B examined under similar conditions.





appear thereafter, while on the other hand, the group B diamond is highly transparent throughout this range. Any attempt to explain these facts should necessarily take into account the facts revealed by the photographs reproduced in Plate I and should be based on sound physical reasoning and not on *ad hoc* suppositions of the kind which one finds frequently in the literature and which can only be described as completely irrational.

### 3. SUMMARY

Approximately ten per cent. of the total number of diamonds form group A and another ten per cent. group B. These two groups exhibit highly contrasting characters. Group A diamonds are isotropic and optically perfect, are opaque to ultra-violet of wavelengths less than  $0.3\mu$  and exhibit a visible blue luminescence. Group B diamonds are visibly birefringent, their transparency extends well beyond  $0.3\mu$  and they are non-luminescent. The two groups differ strikingly in their infra-red behaviour. These facts taken in conjunction indicate that the two groups of diamond differ fundamentally in their crystal structure.



# THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE

## Part III. The Perfect Diamonds and Their Spectral Behaviour

BY SIR C. V. RAMAN

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### 1. INTRODUCTION

A PERFECT diamond should be colourless and transparent and should be free from internal cracks and inclusions and should further exhibit no visible birefringence when placed between crossed polaroids and viewed against a bright source of light. This last test is a stringent one and it serves to exclude a large majority of diamonds. The specimens that do satisfy the test also exhibit the other properties characteristic of the group A diamonds described and illustrated in the second part of this memoir. We shall in the present part deal a little more fully with their optical characters and especially with their infra-red behaviour.

A fine example of a perfect diamond is the tabular crystal in its natural hexagonal form which was presented to the author by the late Dr. Paul Grodzinski. Photographs of this diamond obtained by four different techniques are reproduced in Plate II. The picture marked (a) was obtained with the diamond placed on a fluorescent plate and illumined by the  $\lambda 2536.5$  radiations of a mercury arc which traversed the diamond before reaching the plate. The photograph exhibits the opacity of the diamond to the radiations. The photographs marked (b) was obtained with the diamond held between crossed polaroids and exhibits its perfect freedom from birefringence. The photographs marked (c) and (d) were obtained with the diamond illuminated by sunlight filtered through a plate of Wood's glass. Photograph (c) exhibits the faint blue luminescence of the diamond as seen through a filter of blue glass. The exposure was so prolonged that the luminescence was recorded with great intensity. Photograph (d) represents the luminescent diamond in the same circumstances as viewed through a filter of yellow glass. It will be noticed that the luminescence is then unobservable.

The photographs reproduced in Plate III and marked (a), (b), (c) and (d) were obtained using similar procedures with a cleavage plate of diamond

of Indian origin. It will be noticed that the effects exhibited by it are in each case similar to those seen in Plate II.

## 2. CHARACTERISTIC FEATURES OF THE ABSORPTION

In the first part of this memoir, reference was made to the desirability of recording the transmission curves with the Leitz instrument at a very low speed. The importance of this remark is illustrated by Fig. 1 in the text below which is the record in the  $2\mu$ – $12\mu$  region obtained with a perfect diamond  $0.81$  millimetre thick, the speed of recording being at the rate of 10 minutes per  $\mu$  of wavelength. A comparison with the record of another diamond of the same class but recorded at a speed of 3 minutes per  $\mu$  and reproduced as Fig. 1 in the second part of this memoir shows that the slower speed greatly improves the sharpness and precision of the recording. This is especially evident in the region of wavelengths between  $7\mu$  and  $10\mu$  where the features exhibited by the perfect diamonds make their appearance and which we shall now proceed to discuss.

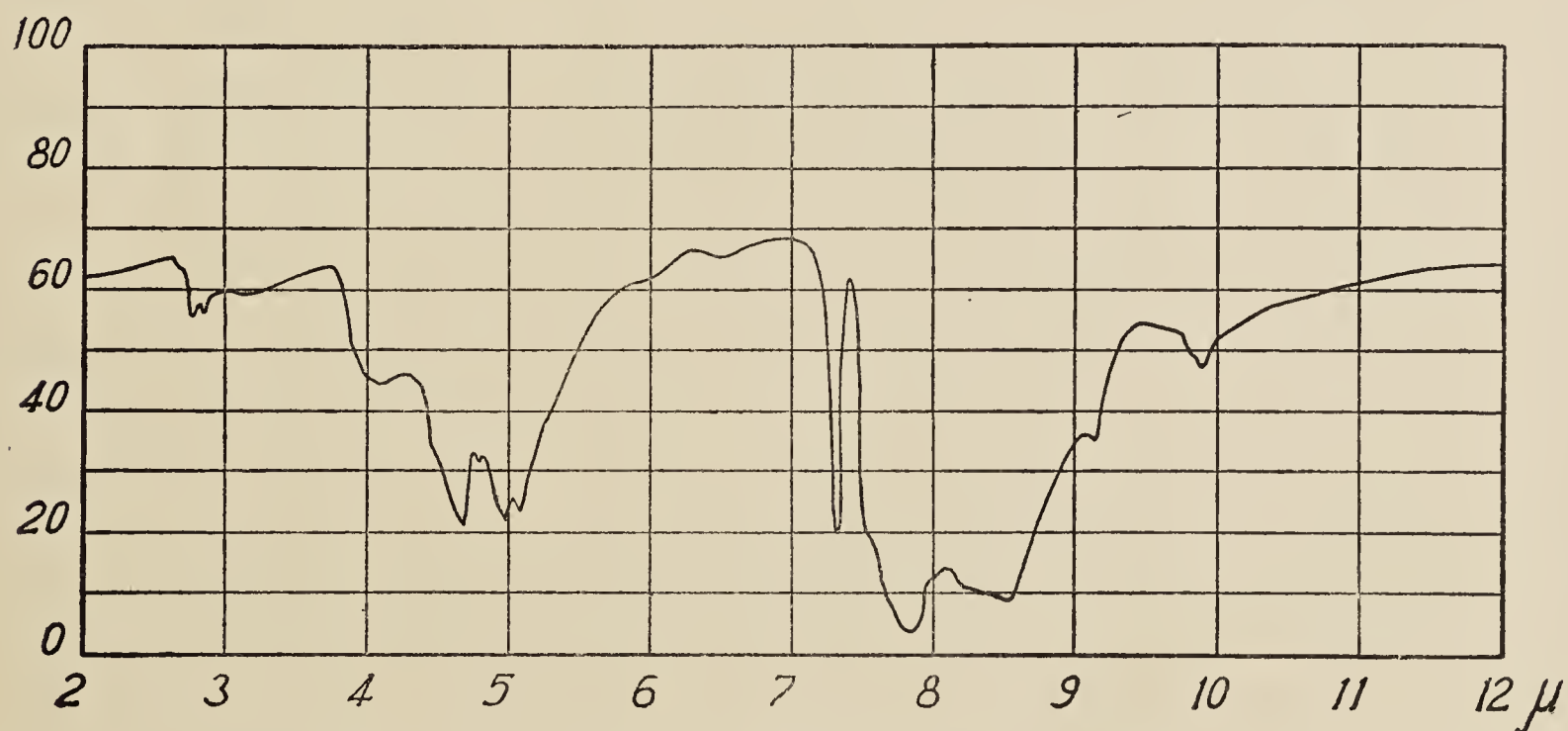


FIG. 1. Percentage Transmission Curve of a Perfect Diamond: (Thickness  $0.81$  millimetre).

A very remarkable feature of the absorption spectra of the perfect diamonds is the sudden increase in absorption which appears between  $7.4\mu$  and  $7.5\mu$ . This is very clearly shown in Fig. 1, the transmission falling from 62 to 20% within a range of only  $0.1\mu$ . The curve coincides with the  $7.5\mu$  ordinate in the region where the transmission falls from 40 to 20% and then suddenly alters its course. The sharp absorption edge at  $7.5\mu$  (or in wave-numbers  $1332\text{ cm.}^{-1}$ ) is thus a highly characteristic feature exhibited by the perfect diamonds. It is well known that in the spectrum of the scattering of light by diamond, a sharply defined frequency shift of  $1332\text{ cm.}^{-1}$



is recorded. This quantitative agreement in respect of frequency makes it evident that in both cases we are concerned with effects arising out of the structure of diamond itself.

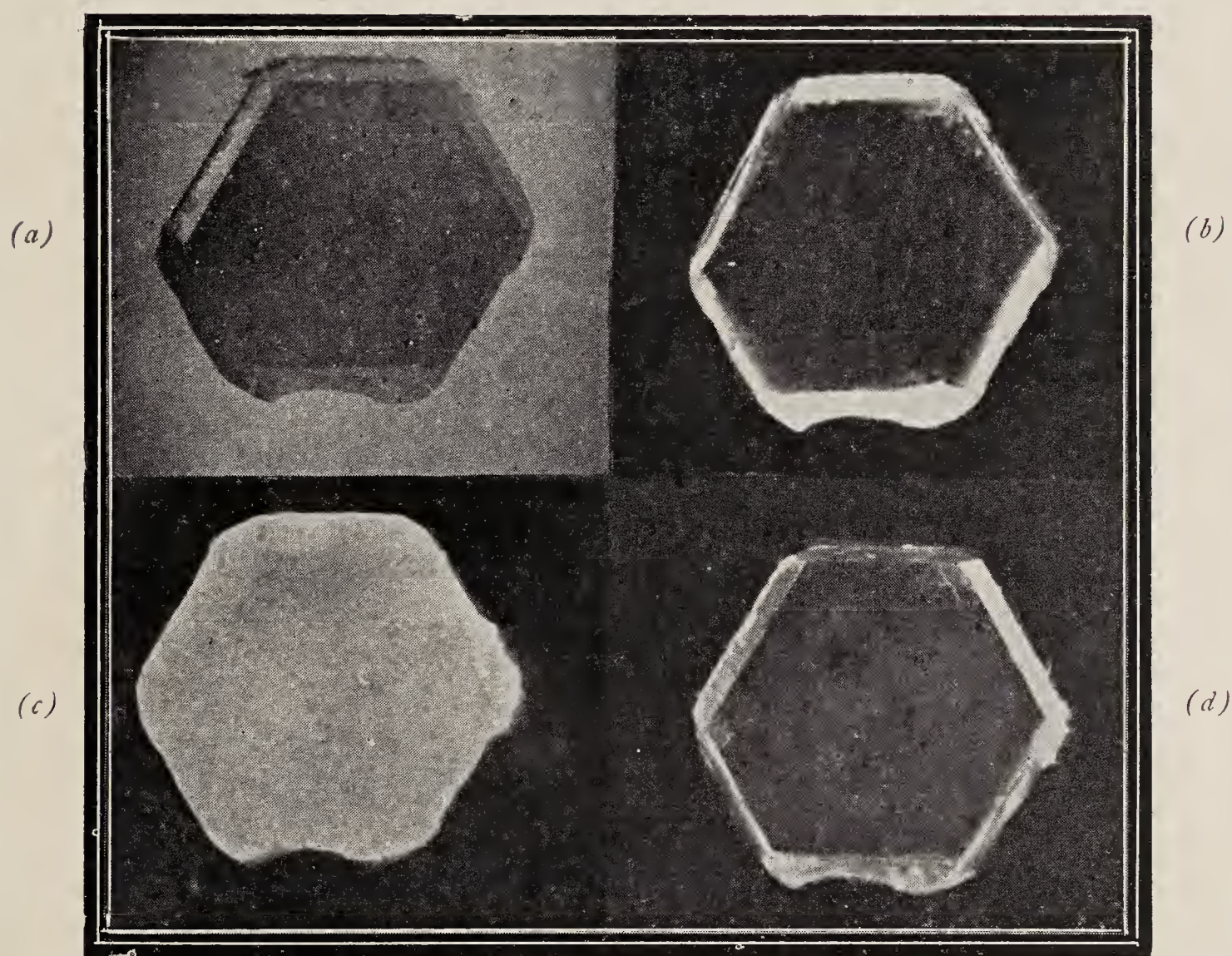
Besides the edge at  $7.5\mu$ , the record reproduced as Fig. 1 shows other well-marked features at longer wavelengths, *viz.*, an absolute minimum of transmission at  $7.85\mu$ , a sharp turn in the course of the record at  $8.2\mu$ , another very sharp turn at  $8.5\mu$ , another turn followed by a very steep rise at  $9.2\mu$  and finally a well-defined peak at  $9.9\mu$ . Diamond thus exhibits in its absorption spectrum in this range six clearly defined features at  $7.5\mu$ ,  $7.85\mu$ ,  $8.2\mu$ ,  $8.5\mu$ ,  $9.2\mu$  and  $9.9\mu$  respectively. Expressed as frequencies in wave-numbers, these are at 1332, 1273, 1219, 1176, 1087 and 1010  $\text{cm}^{-1}$  respectively. The appearance of these features in infra-red absorption would be accounted for if the crystal structure had specific vibrational modes having the frequencies listed and the radiations traversing diamonds of this class excited such vibrations. In other words, the region of wavelengths between  $7.5\mu$  and  $10\mu$  exhibits the infra-red absorption spectrum of the first order of the perfect diamonds.

### 3. THE ABSORPTION SPECTRA OF HIGHER ORDERS

Since, as we have seen, the first-order absorption spectrum commences at  $1332\text{ cm}^{-1}$  and extends towards lower frequencies, the second-order spectrum exhibiting the first overtones of the fundamental frequencies should commence at  $2664\text{ cm}^{-1}$  and extend towards lower frequencies. Likewise, the third-order spectrum should commence at  $3996\text{ cm}^{-1}$  and continue to lower frequencies. The same limits expressed as wavelengths are  $7.5\mu$ ,  $3.75\mu$  and  $2.5\mu$  respectively. Actually, it is seen from Fig. 1 above that there is a large and sudden drop in the percentage transmission at about  $3.75\mu$  and another but less conspicuous drop in transmission at about  $2.6\mu$ . It is thus evident that the perfect diamonds exhibit the complete absorption spectrum including the first, second and third orders at the appropriate wavelengths and frequencies.

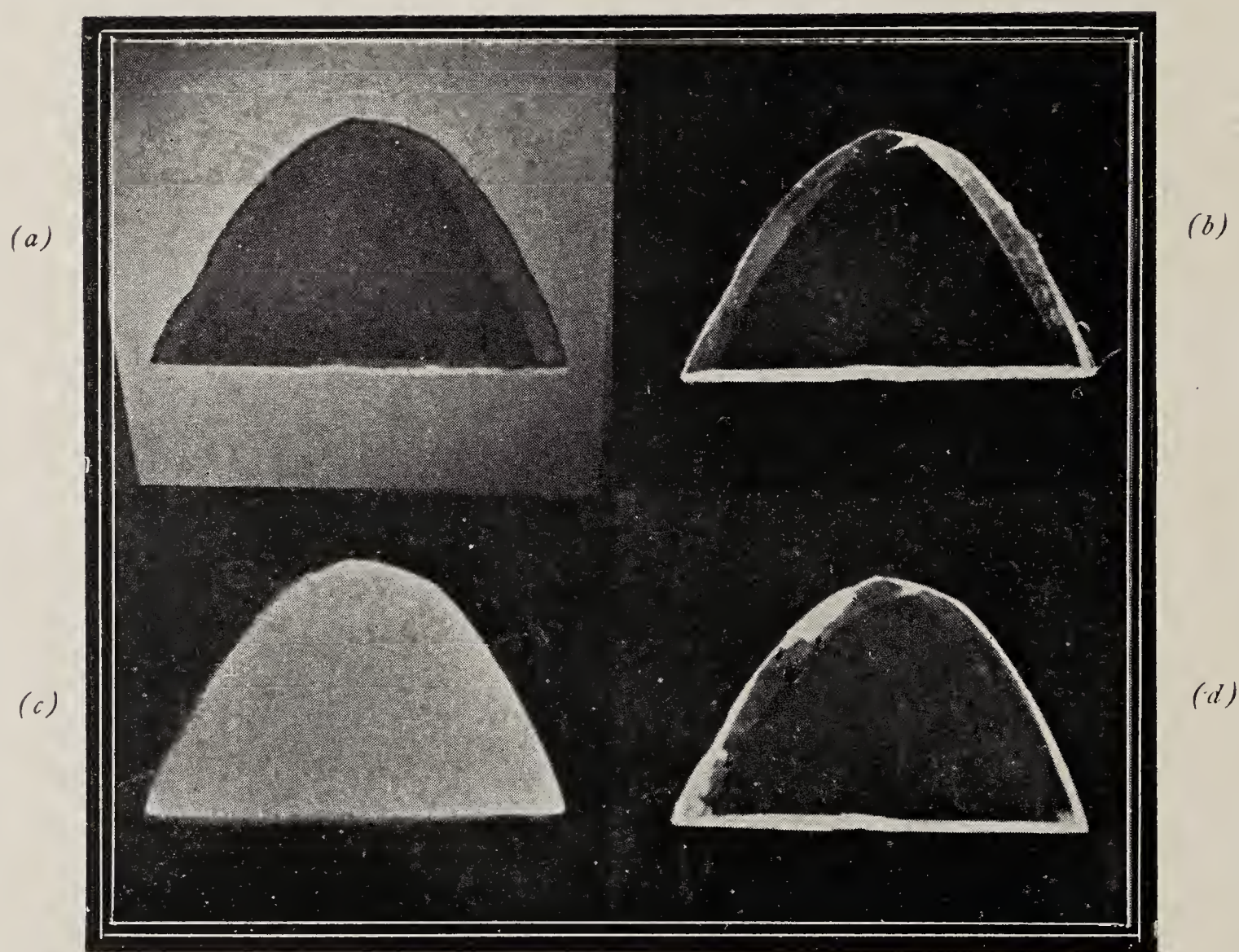
We may here draw attention to the most conspicuous features in the second-order spectrum, *viz.*, the extremely sharp minimum of transmission at  $4.60\mu$  or  $2174\text{ cm}^{-1}$ , the double peak at  $4.95\mu$  and  $5.09\mu$  or  $2020\text{ cm}^{-1}$  and  $1965\text{ cm}^{-1}$ . We may also draw attention to the sudden fall in transmission from 68% at  $7\mu$  to 21% at  $7.30\mu$  followed by an equally sudden rise to 62% at  $7.40\mu$ . This very remarkable feature in the second-order spectrum evidently stands in a close physical relationship to the sharp absorption edge at  $7.5\mu$  appearing in the first-order spectrum, as is shown





A Perfect Diamond (tabular crystal)





A Perfect Diamond (cleavage plate)



by the fact that it does not appear in the case of group B diamonds which show only the second and third-order spectra, and not that of the first order. As will be explained in a subsequent part of this memoir, the sharp dip at  $7.30\ \mu$  or  $1370\ \text{cm.}^{-1}$  is the result of the excitation of a summation of the two lowest, viz., the seventh and eighth vibrational frequencies of the diamond structure which are at  $746\ \text{cm.}^{-1}$  and  $624\ \text{cm.}^{-1}$  respectively ( $13.40\ \mu$  and  $16.02\ \mu$  when expressed as wavelengths). The summational frequency is powerfully excited in absorption by reason of its close contiguity to the principal  $1332\ \text{cm.}^{-1}$  frequency which is active in the perfect diamonds.

It may also be remarked that the sharp peaks at  $2174\ \text{cm.}^{-1}$  and  $2020\ \text{cm.}^{-1}$  are the octaves of the fifth and sixth vibrational frequencies of diamond which, as we have already noticed, manifest themselves clearly as fundamentals in its first-order absorption spectrum. The third sharply defined peak at  $1965\ \text{cm.}^{-1}$  results from a summation of two fundamental frequencies of vibration, viz.,  $1219\ \text{cm.}^{-1}$  and  $746\ \text{cm.}^{-1}$  respectively.

The various sharply defined features observed in the second-order absorption of diamond are thus a clear demonstration that the *atomic nuclei in the structure of diamond possess a set of free vibrational modes with discrete monochromatic frequencies*. On the other hand, the infra-red absorption spectrum represents the *forced vibrations* of the structure produced by the field of the incident radiation acting on the electrons which hold the nuclei in place. It is necessarily recorded as a continuous curve exhibiting peaks or sharp turns or sudden drops at positions determined by the nuclear vibration frequencies.

#### 4. SUMMARY

The perfect diamonds exhibit an absorption which is readily recognised as including the first, second and third order spectra. From the features observed in these spectra it is inferred that the diamond structure has eight discrete frequencies of free vibration, viz., 1332, 1273, 1219, 1176, 1087, 1010, 746 and  $624\ \text{cm.}^{-1}$ . The fifth and the sixth frequencies appear very prominently with doubled frequency as sharp peaks in the second-order absorption spectrum, while a summation of the seventh and eighth frequencies is recorded with extraordinary strength and sharpness by reason of its contiguity to the active fundamental of highest frequency.



# THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE

## Part IV. The Non-Luminescent Diamonds

BY SIR C. V. RAMAN

(Memoir No. 129 of the Raman Research Institute, Bangalore-6)

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### 1. INTRODUCTION

THE special properties which distinguish group B diamonds from the group A or perfect diamonds have already been described and illustrated in the second part of this memoir. Photographs of individual diamonds of the group B class on a somewhat larger scale are however needed to exhibit these properties in an adequate fashion. Accordingly, enlarged pictures of two of these diamonds have been reproduced in Plate IV. Both of these diamonds are polished plates. While the semicircular diamond has rough edges, the other is a diamond cut into a rectangular shape and its edges as well as its faces given a good polish.

The two photographs marked (a) and (a) in Plate IV exhibit a property characteristic of the group B diamonds, viz., their transparency to the  $\lambda$  2536.5 radiations of the mercury arc. The radiations traversed the diamonds before reaching the fluorescent plate on which they were placed. The perfect transparency of the diamonds to the ultra-violet radiations is displayed by the fluorescence of the supporting plate in the areas covered by the diamond and the areas not so covered being of equal intensity. It may be remarked that the transparency of the diamonds of group B to the  $\lambda$  2536.5 radiations is of great importance from a practical point of view. For, it enables these diamonds to be used for studies of the spectrum of light-scattering with the resonance radiation from a water-cooled magnet-controlled mercury arc as the exciter. The second-order spectrum of light-scattering in diamond can then be successfully recorded.

As has already been noted in the first part of this memoir, the group B diamonds present a striking contrast with group A or perfect diamonds in exhibiting a readily observable birefringence. This effect was illustrated in Plate I accompanying the second part of this memoir, but the photographs were on much too small a scale to reveal the real nature of the phenomenon. The photographs now reproduced as (b) and (b) in Plate IV are on a larger



scale. Crossing the irregular dark and bright areas can be glimpsed numerous parallel streaks of varying brightness. A still larger magnification is, however, needed fully to exhibit the character of the birefringence. In Plate V is reproduced an enlargement of the birefringence pattern of a plate of diamond 14 mm. by 9 mm. in size and 1.47 mm. in thickness. On the same scale below it is reproduced a photograph exhibiting the ultra-violet transparency of the diamond. It may be remarked neither in Plate IV (b) and (b) nor in Plate V (b) does the smallest trace of the structures so clearly seen in the birefringence pattern come into evidence in the ultra-violet transparency, though the latter was observed and photographed under conditions entirely favourable for exhibiting the variations of transparency over the area of the diamond, had they been present.

Finally, we may draw attention to the photographs of the two diamonds marked (c) and (c) in Plate IV. These exhibit the complete absence of any luminescence of these diamonds under ultra-violet illumination.

## 2. THE INFRA-RED ABSORPTION SPECTRA

The transparency of the group B diamonds in the ultra-violet region of the spectrum around  $0.25\mu$  as contrasted with the opacity of the group A diamonds in the same region goes hand in hand with the absence in the group B diamonds of the characteristic absorption between  $7\mu$  and  $10\mu$  in the infra-red conspicuously exhibited by the group A diamonds. The relationships between the spectral behaviour of group A and of group B diamonds in the near ultra-violet and in the near infra-red are so clear and quantitatively so definite as to leave no doubt that the explanation in both cases has to be sought for on the same lines, viz., a fundamental difference in the structure of the diamonds in the two groups. We shall return to this subject later on and shall meanwhile describe and illustrate the infra-red behaviour of group B diamonds a little more fully than before.

Figure 1 below is the record of the percentage of transmission in the region between  $2\mu$  and  $12\mu$  of a non-luminescent diamond plate of thickness of 1.07 mm. Figure 2 is a record with the same plate for the region between  $13\mu$  and  $24\mu$ , and it will be noticed that this is practically featureless. From the two records taken together, it is evident that if we take into account the loss by reflection at the two faces of the plate, these diamonds exhibit a practically complete transparency over the entire wavelength range between  $7\mu$  and  $24\mu$ . On the other hand, between  $2\mu$  and  $6\mu$ , they exhibit a very marked absorption which may be identified with the second-order and third-order spectra of diamond, the first-order being totally absent. We may



compare these with the features noticed in the same region of wavelengths in Fig. 1 in the text of the third part of the memoir. That figure was the record of a perfect diamond showing all the three orders of absorption. In the region between  $2\mu$  and  $6\mu$ , the two figures are practically indistinguishable from each other. In particular, the sharply defined minima of transmission appear, within the limits of accuracy of the recording mechanism, at the same positions in both cases.

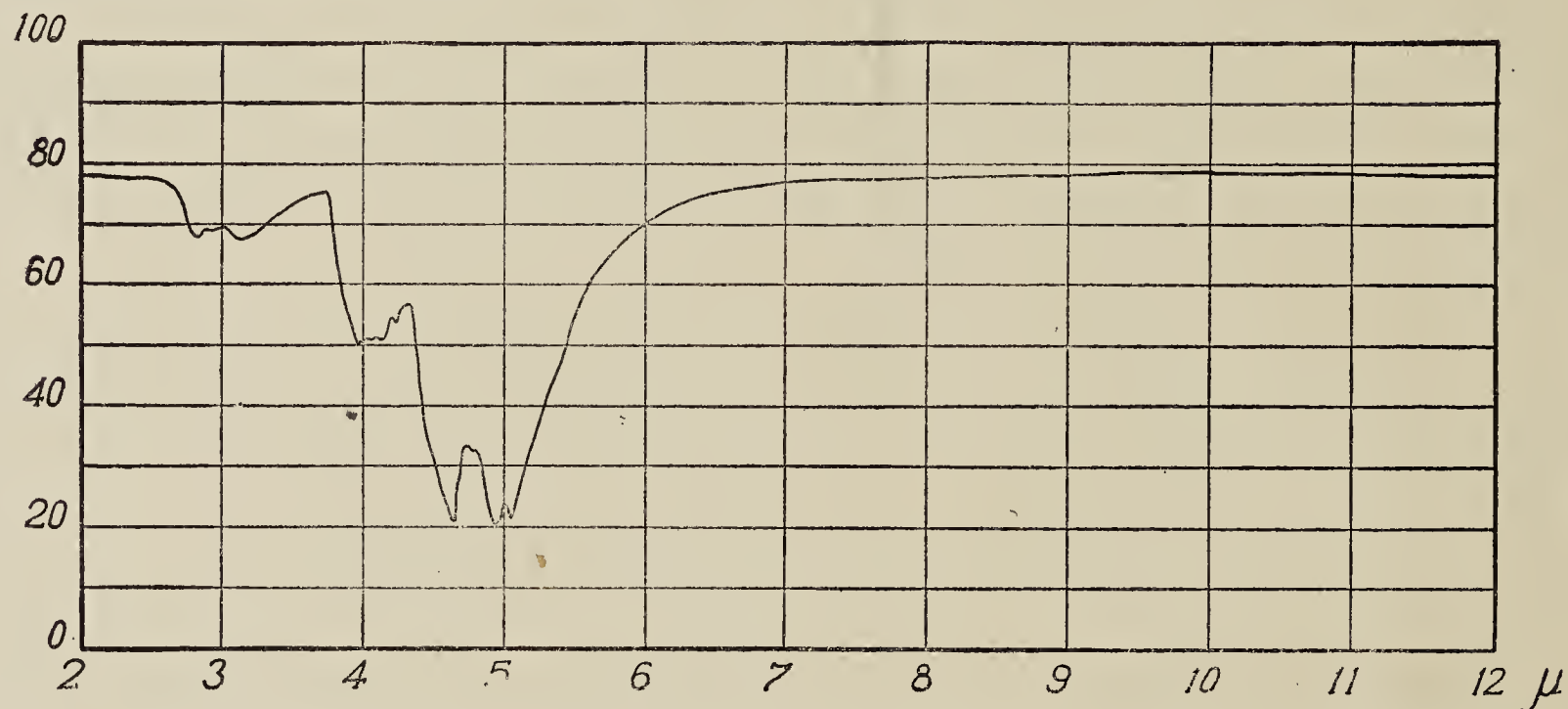


FIG. 1. Transmission Percentages of a Non-Luminescent Diamond. (Thickness 1.07 millimetres).

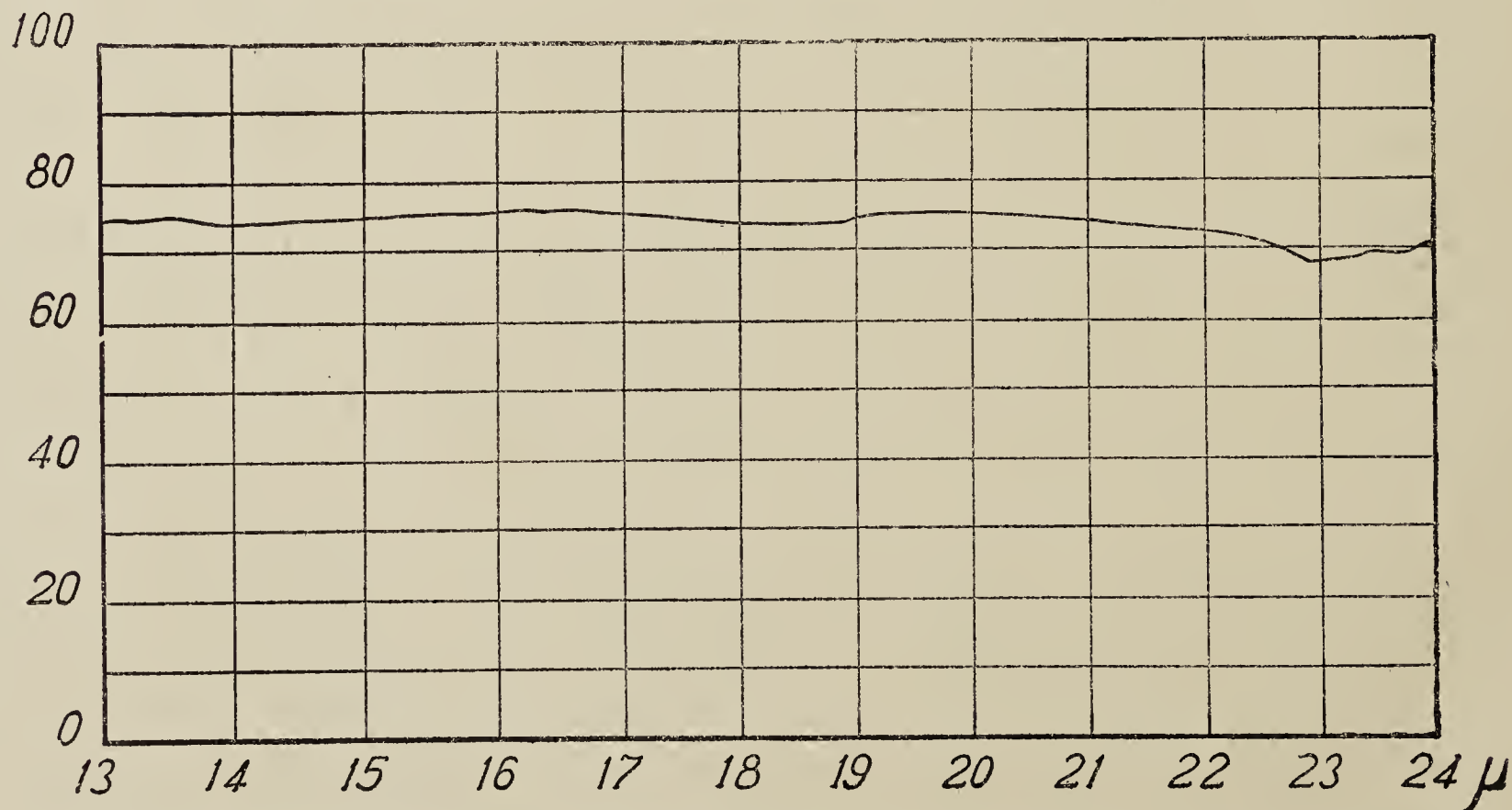


FIG. 2. Transmission Percentages of a Non-Luminescent Diamond. (Thickness 1.07 millimetres).

We may here remark that the features appearing in the second-order absorption spectra are very clearly related to the features in the first-order absorption recorded with the perfect diamonds. Some of these relationships

have already been pointed out in the previous part of the memoir and we may here usefully draw attention to a few others. The steep fall in the transmission percentage which commences at  $3.75\mu$  and terminates at  $4\mu$  has its counterpart in the first-order absorption of the perfect diamonds which rises quickly and reaches its highest values in the wavelength range between  $7.5\mu$  and  $8\mu$ . The steep increase in absorption which commences at  $4.3\mu$  and culminates at the sharp minimum at  $4.62\mu$  in the second-order spectrum has its counterpart in the first-order in the steep increase in transmission which commences at  $8.55\mu$  and after a brief arrest at  $9.15\mu$  continues again beyond that wavelength. Then again, the fall in absorption between the two sharp peaks located at  $4.62\mu$  and  $4.95\mu$  appearing in the second-order absorption has its counterpart in the first-order absorption in the increased transmission appearing in the region between  $9.2\mu$  and  $9.9\mu$ . These quantitative correspondences between the spectra of the two orders indicate that both spectra are based on the excitation of the same set of vibrational modes with discrete frequencies, though the activities of these modes in the first order and the second order may be altogether different. Indeed, it is clear from the facts that the fifth and sixth vibrational modes are those exhibiting the greatest infra-red activity in the second order, whereas in the first-order absorption, when it is manifested, the first few modes are far more active than all the others.

### 3. NATURE AND ORIGIN OF THE BIREFRINGENCE

We may next proceed to describe and discuss the patterns of birefringence which the non-luminescent diamonds exhibit. To observe the patterns, it is a convenient procedure to place the diamond on a glass plate which can be rotated between two crossed polaroids and to view the specimen through a magnifier of suitably chosen power. As the plates of diamond are usually not very thick, it is possible to use a high-power lens and this is indeed necessary to obtain a correct idea of the characters of the birefringence.

All the diamonds of the non-luminescent class in the author's collection have been examined and their birefringence patterns have been found to exhibit certain general characteristics. The restoration of light which is observed is not uniform over the area of the diamond but is seen resolved into a series of parallel bands which are alternately dark and bright. These bands run continuously across the diamond from periphery to periphery. In nearly all the cases, one notices two sets of such bands cutting across each other, but they are not always equally prominent. As the diamond is rotated between the crossed polaroids, each set of bands disappears when it is parallel



to the plane of polarisation of the polariser or of the analyser, and is seen most clearly when it bisects the angle between them. In the cases when the two sets of bands cut each other at right angles, they appear and disappear simultaneously as the diamond is rotated.

Examined under the higher magnifications, the bands in the pattern appear as bundles of fine thread-like lines of light. By reason of their criss-crossing, the pattern has a lace-like appearance. Due to the criss-crossing also, the threads exhibit a wavy outline and are not perfectly straight. Some idea of these effects can be gathered from the photographs reproduced in Plates IV and V accompanying this part of the memoir.

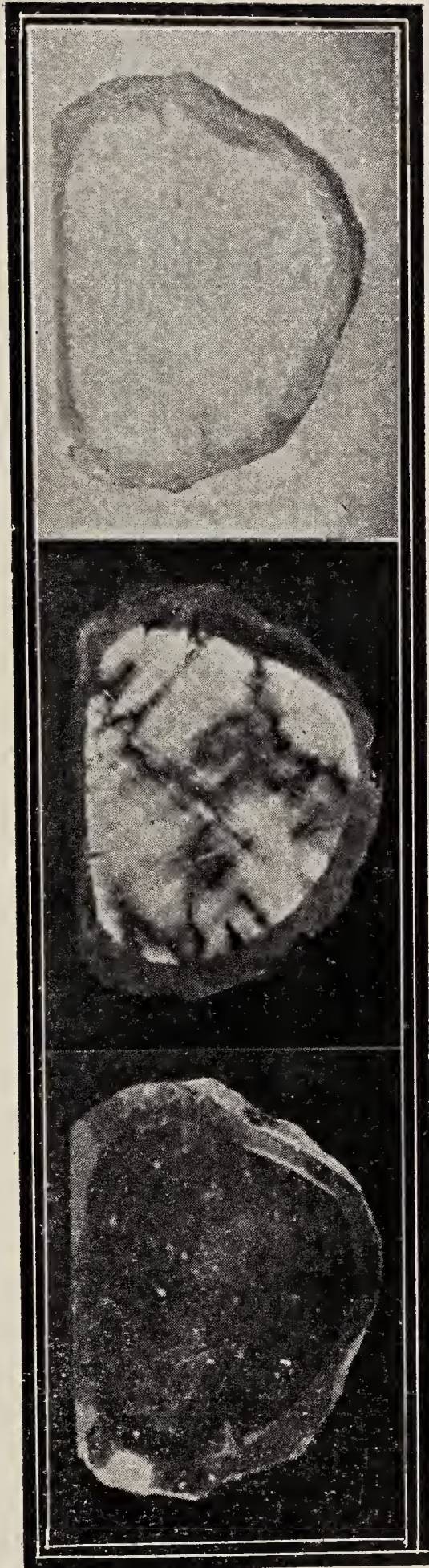
The mutual orientation of the two sets of bands and their alignment with respect to the crystal structure are obviously matters of importance. In some of the plates, they are seen to be mutually perpendicular, while in others they run at an angle to each other which is approximately sixty degrees. To determine their crystallographic orientation, it is necessary to know the orientation of the plate of diamond in which they are seen. In this connection a reference should be made to the thorough and painstaking studies carried out by G. N. Ramachandran on the birefringence of diamonds (*Proc. Ind. Acad. Sci., Sec. A*, Vol. 24, page 65, 1946). Ramachandran's investigations covered not only the diamonds of the non-luminescent class but also the composite diamonds which will form the subject of the fifth part of this memoir. Using a petrographic microscope in conjunction with a Federov universal rotating stage, he discovered that the structural birefringence observed in diamond has its origin in the presence of laminations in the structure which are orientated parallel to the octahedral planes or to the dodecahedral planes of the crystal or to both. He also determined the magnitude of the birefringence in various cases. His observations with the non-luminescent diamonds were particularly significant. They showed clearly that the birefringence pattern exhibited by such plates when viewed normally between crossed polaroids arises from a lamellar structure of the kind referred to. Why such a lamellar structure is present in diamonds of this class associated with the various other properties described earlier is a question the answer to which is evidently to be found in the basic facts of the architecture of the diamond crystal.

#### 4. SUMMARY

The non-luminescent diamonds exhibit the infra-red absorption spectra of the second and third orders, while the first order is totally absent. A critical examination of the spectrographic records shows clearly that the second-



(a)



(b)

(c)

(a)

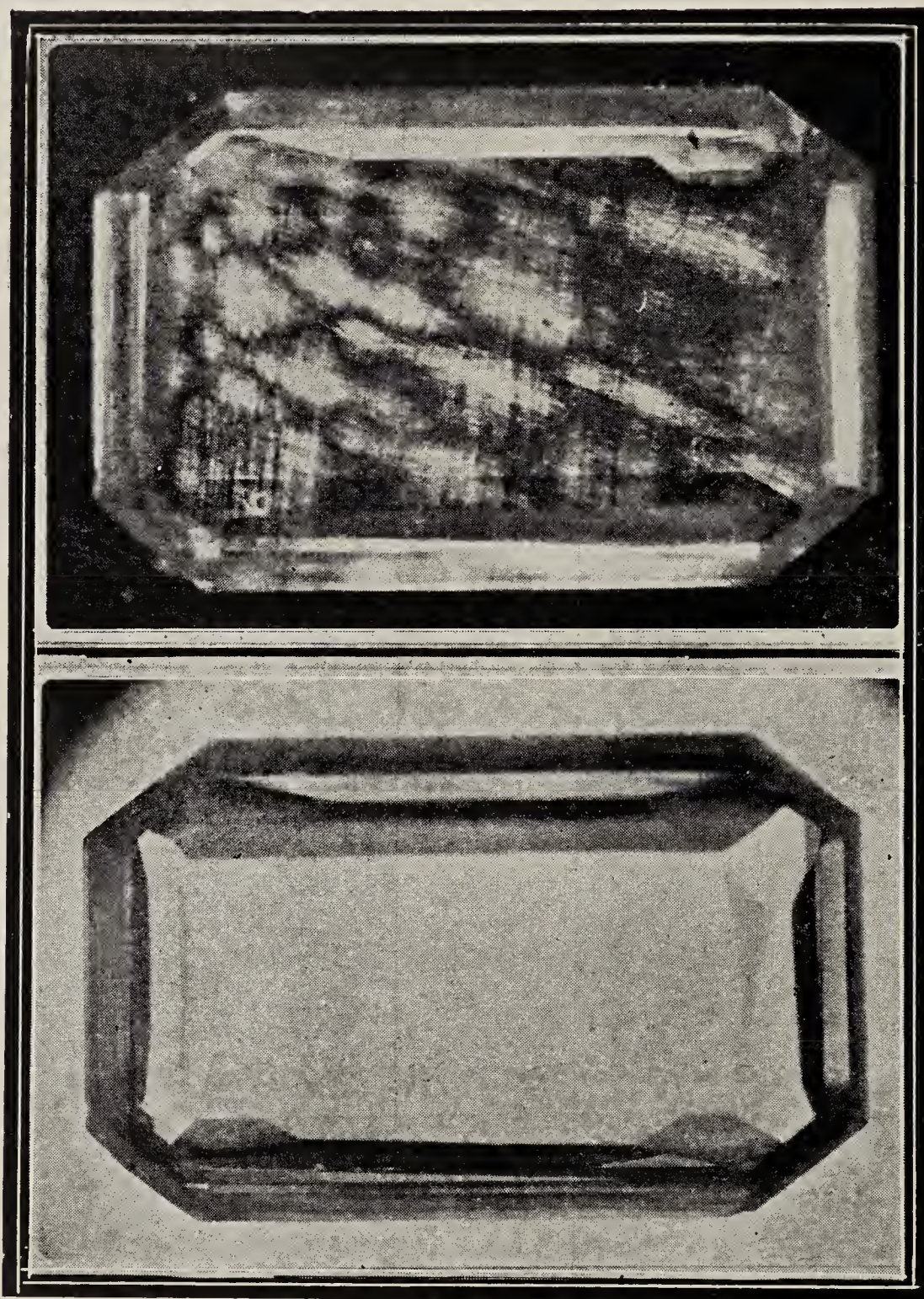


(b)

(c)

Two Non-luminescent Diamonds





(a)

(b)

(a) Birefringence and (b) Ultra-violet transparency.



order spectrum is based on the same vibrational modes with discrete frequencies as the first, the activities of the modes, however, being different in the two cases.

The non-luminescent diamonds exhibit a type of birefringence which arises from the presence in them of laminations orientated parallel to the octahedral planes or to the dodecahedral planes of the crystals or to both.



# THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE

## Part V. The Composite Diamonds

BY SIR C. V. RAMAN

(Memoir No. 129 of the Raman Research Institute, Bangalore-6)

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### 1. INTRODUCTION

THE many striking differences in the physical behaviour of the perfect diamonds and of the non-luminescent diamonds are a sufficient demonstration that their crystal structures are fundamentally different. Nevertheless, their structures must be closely related to each other. For, they have infra-red absorption spectra which in the second and third orders are indistinguishable, while the first order is present only for the perfect diamonds and absent for the non-luminescent ones. Spectroscopic theory considered in the light of the mechanism of infra-red absorption gives us the clue to the origin of these differences. But the differences are evidently not of such a nature as to preclude the two structures appearing in juxtaposition in one and the same diamond. Indeed, this is so frequently the case that the composite diamonds, as we shall call them, form the large majority amongst the polished plates of diamond in the writer's collection. As has already been mentioned, about ten per cent. of the specimens are perfect diamonds, another ten per cent. are non-luminescent ones, while the remaining eighty per cent. are composite diamonds.

### 2. PROOFS OF THE COMPOSITE NATURE

The easiest and also the most convincing demonstration that any particular specimen is a composite diamond is furnished by observations of its ultra-violet transparency. The technique of such observations has already been described. The  $\lambda$  2536.5 radiation of a mercury arc lamp passes through the diamond and is then incident on a fluorescent plate in close contact with it. The luminescence of the plate then immediately reveals the variations in the transparency of the diamond over the different parts of its area.

Another very instructive demonstration of the composite nature of a diamond is furnished by observations of the luminescence excited by ultra-violet radiation. Such luminescence may be observed either through a filter which transmits only the blue end of the spectrum or through a yellow filter



which cuts out the blue and green altogether and transmits only the yellow, orange and red. The characters of the luminescence are found to be totally different as observed through the two filters and these differences are very revealing in respect of the structure of the diamond.

Still another method of observation is to view the diamond between crossed polaroids against a bright source of light. A perfect diamond would, of course, exhibit no birefringence. A non-luminescent diamond, on the other hand, would exhibit a birefringence of the kind described in the fourth part of this memoir, but no trace of the structure thus revealed would appear in its ultra-violet transparency. Composite diamonds, on the other hand, exhibit birefringence patterns of which the features can be recognised both in the ultra-violet transparency patterns and in the patterns of luminescence, and especially in the latter as seen through a yellow filter.

Seven polished plates of diamond in the writer's collection have been photographed by each of the four methods described above. These photographs are reproduced respectively in Plates Nos. VI, VII, VIII, IX, X, XI and XII. In each case, the picture marked (a) exhibits the variations of the ultra-violet transparency, that marked (b) exhibits the blue luminescence, that marked (c) the yellow luminescence and that marked (d) the birefringence pattern as observed with a chosen orientation of the diamond between the crossed polaroids.

The composite nature of a diamond is also revealed by the spectrographic record of its infra-red transmission. Figures 1 and 2 below reproduce these records respectively for the two plates of diamond of which the photographed patterns appear in Plate VI and in Plate VII. From Plate VI (a) and (b), it is evident that the greater part of the oval area of this diamond is of the non-luminescent kind transparent in the ultra-violet. Two sharply-defined areas, one large and another small, having the form of equilateral triangles are however seen in these figures which exhibit an opacity in the ultra-violet as well as a bright blue luminescence. The preponderance of non-luminescent diamond in this specimen is very clearly exhibited by the spectrographic record reproduced as Fig. 1 below. This shows the first-order absorption between  $7\mu$  and  $10\mu$  only very weakly as compared with the absorption of the second order.

On the other hand, it is evident from Plate VII (a) and (b) that a large part of the area of the diamond figured in it is ultra-violet opaque and blue-luminescent, while the rest is ultra-violet transparent and non-luminescent. It is, therefore, not surprising that in Fig. 2 which is its spectrographic chart,



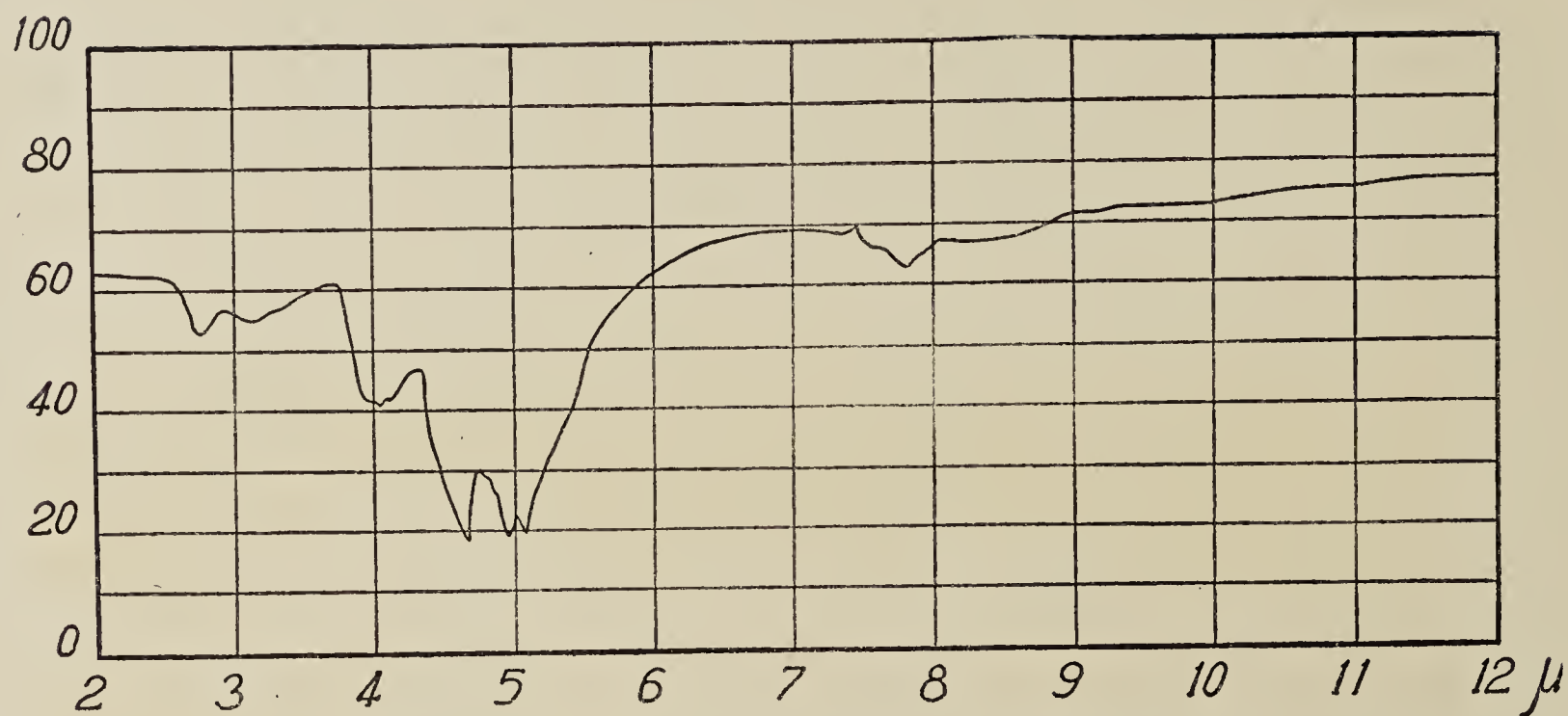


FIG. 1. Infra-Red Absorption by Composite Diamond (Thickness 0.83 millimetre).

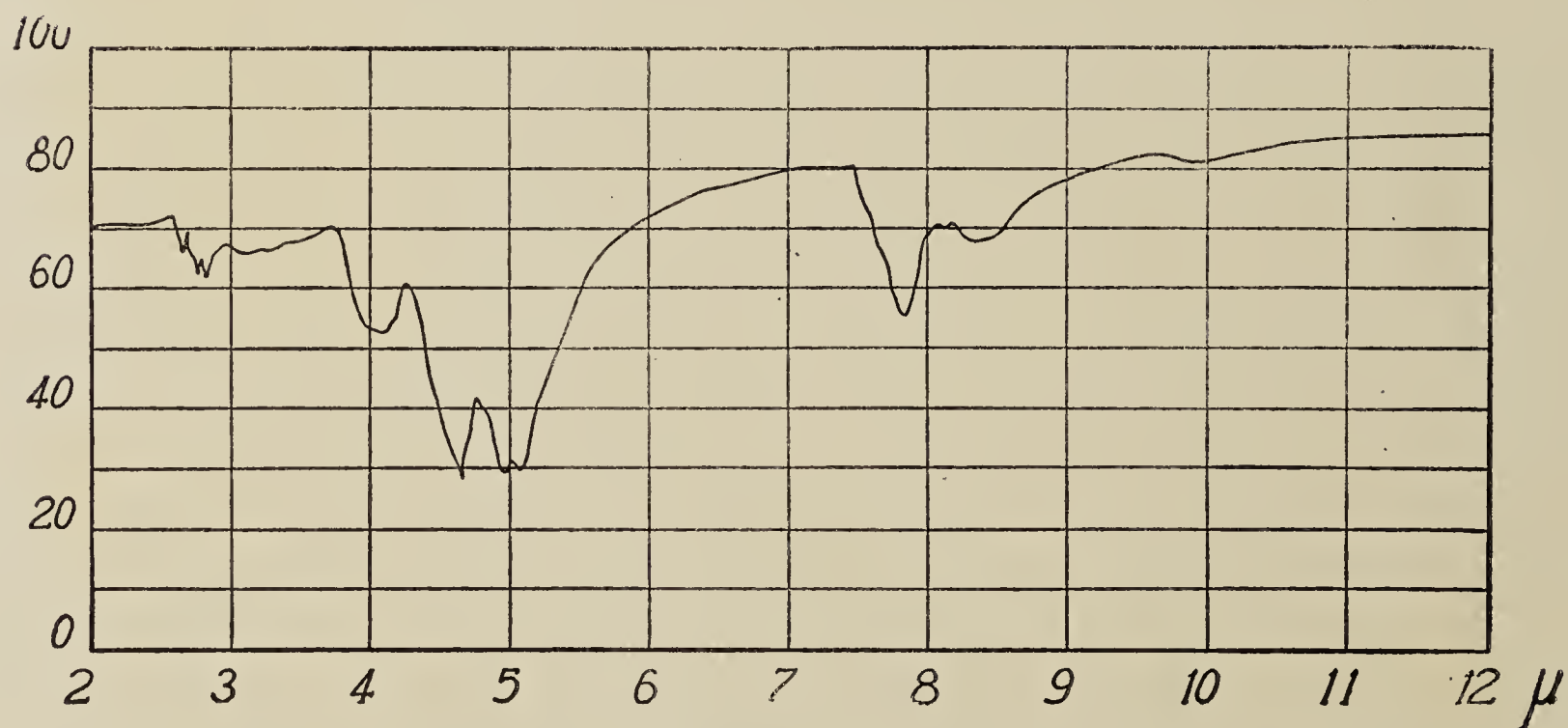


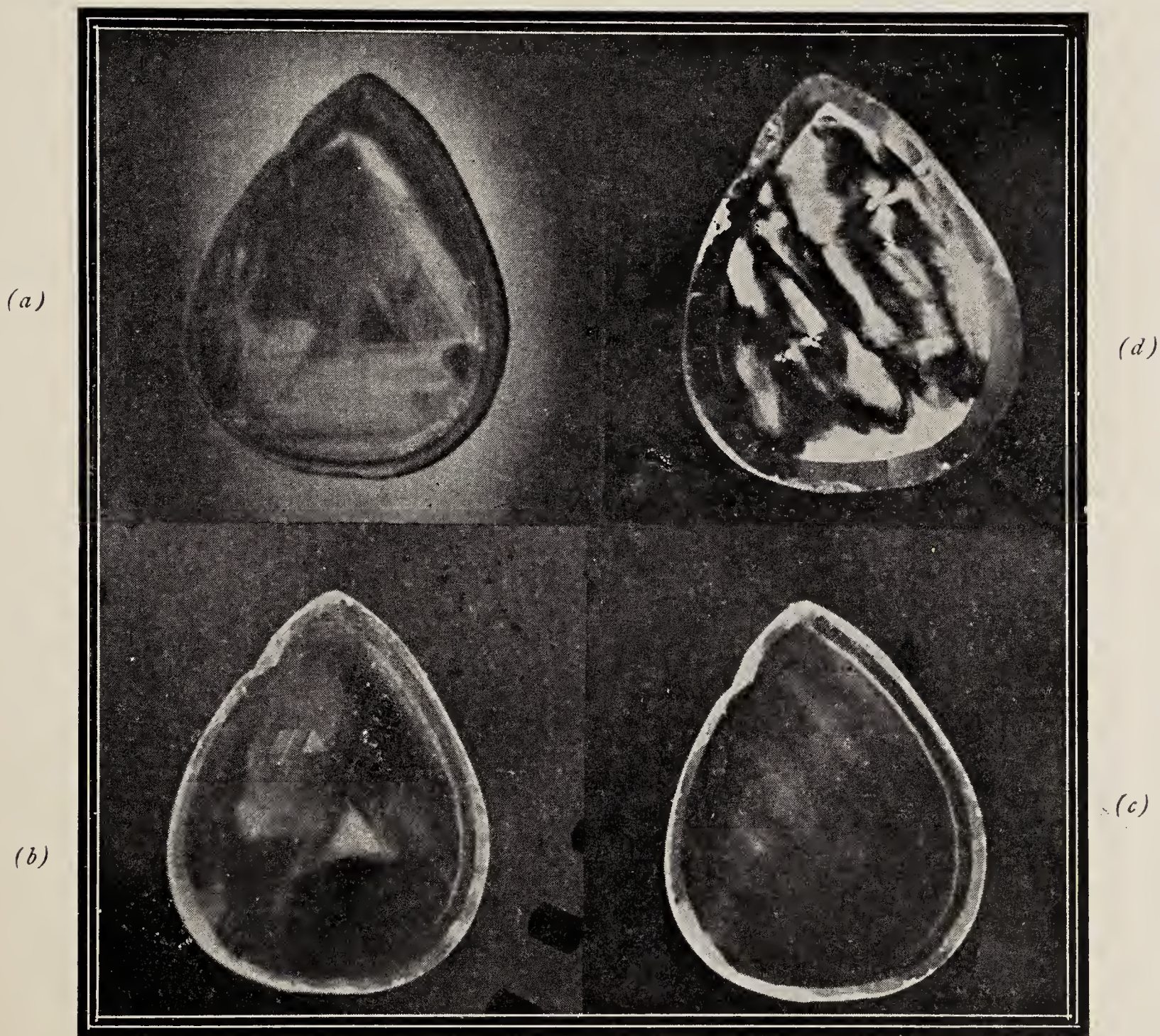
FIG. 2. Infra-Red Absorption by Composite Diamond (Thickness 0.81 millimetre).

the first-order infra-red absorption between  $7\mu$  and  $10\mu$  is more strongly manifested than in Fig. 1.

### 3. THE GEOMETRIC CHARACTER OF THE PATTERNS

Examining in detail the ultra-violet transparency and blue-luminescence patterns of the several diamonds reproduced in Plates VI, VII, VIII, IX, X, XI and XII, the most striking features exhibited by them are firstly the correlations between these properties manifest in the patterns, and secondly the geometric character of the patterns which is clearly related to the orientation of the octahedral or dodecahedral planes in the crystal with respect to the surfaces of the plate.

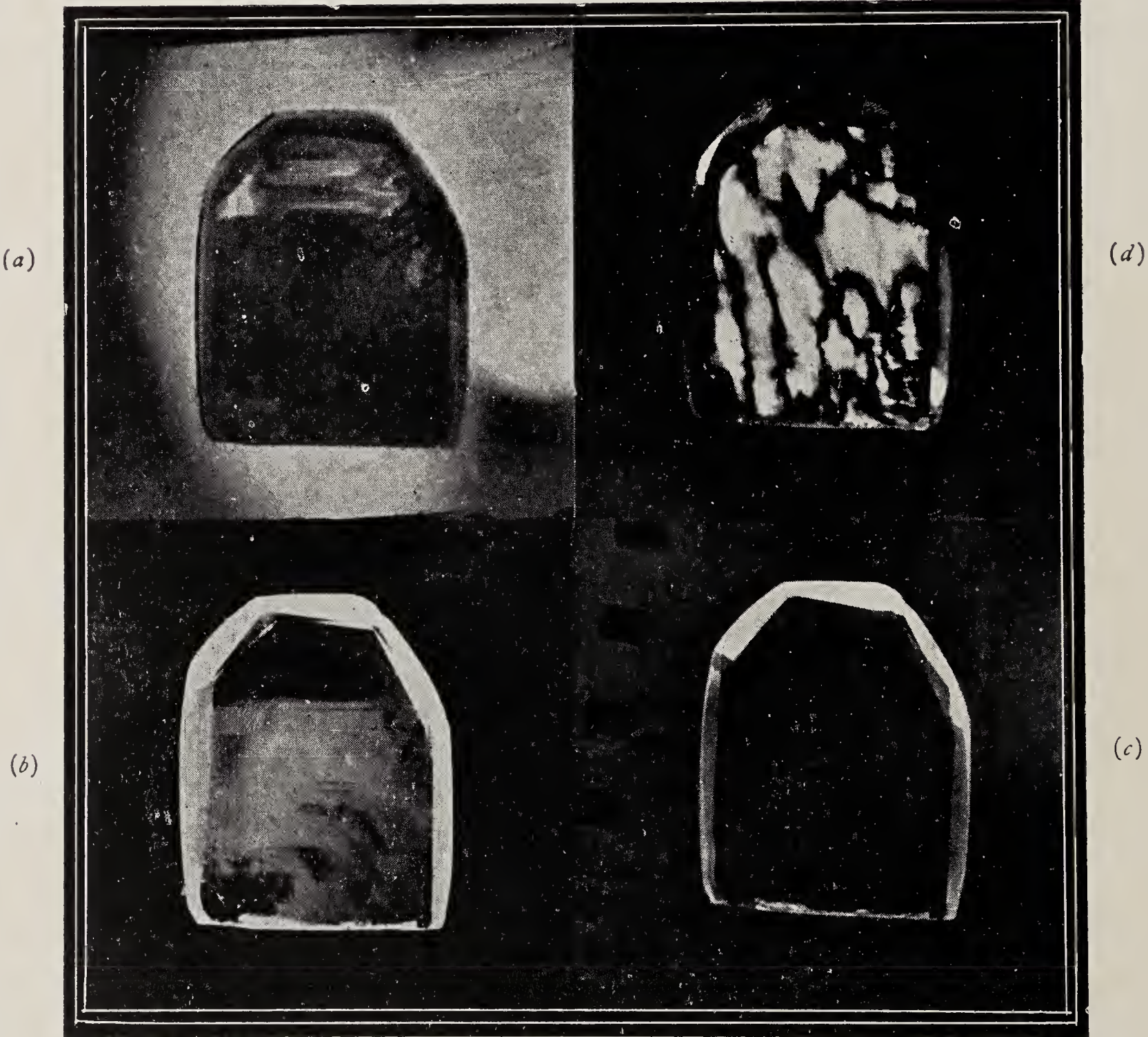




(a) Ultra-violet transparency  
(c) Yellow luminescence

(b) Blue luminescence  
(d) Birefringence

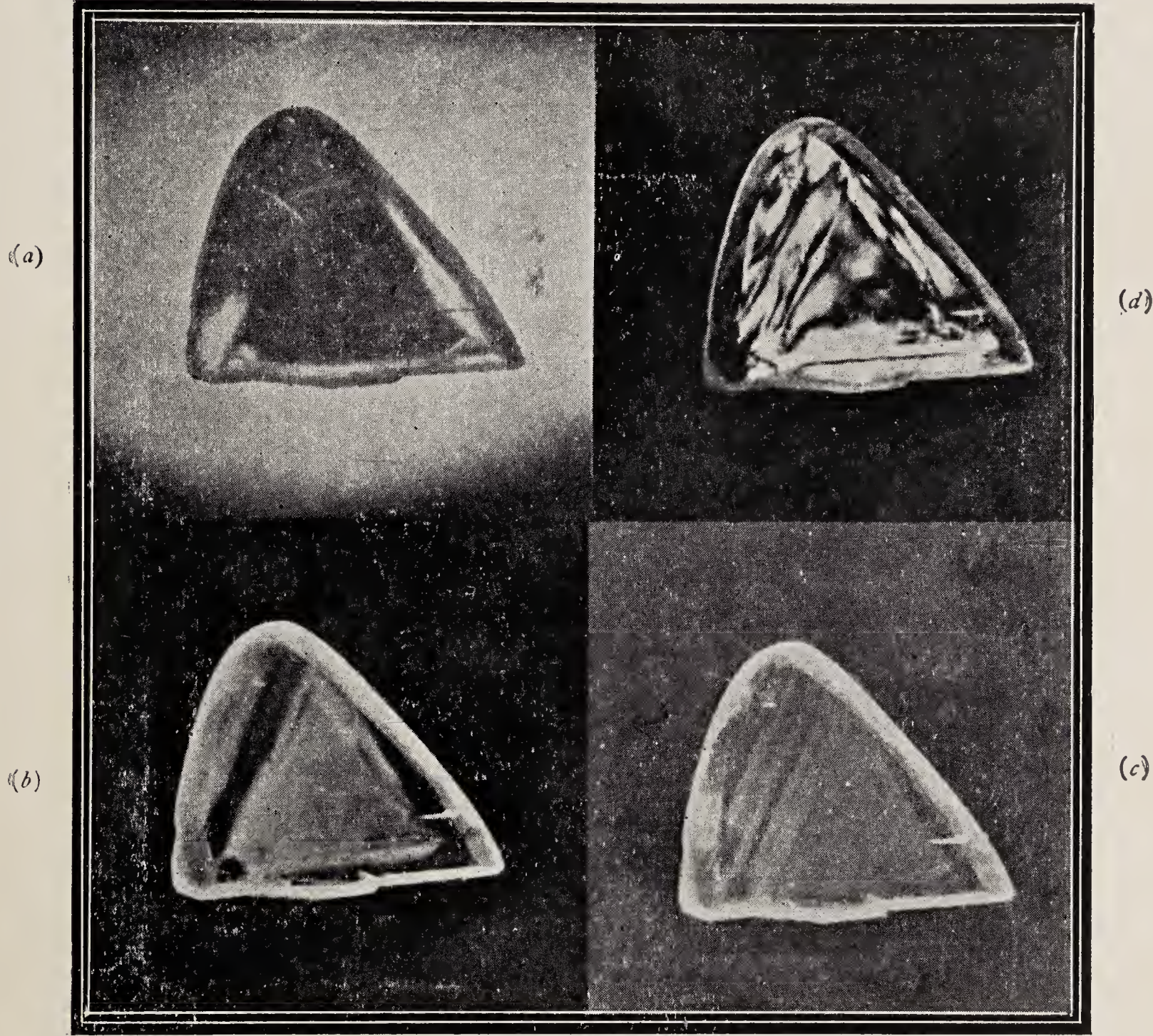




(a) Ultra-violet transparency  
(c) Yellow luminescence

(b) Blue luminescence  
(d) Birefringence





(a) Ultra-violet transparency  
(c) Yellow luminescence

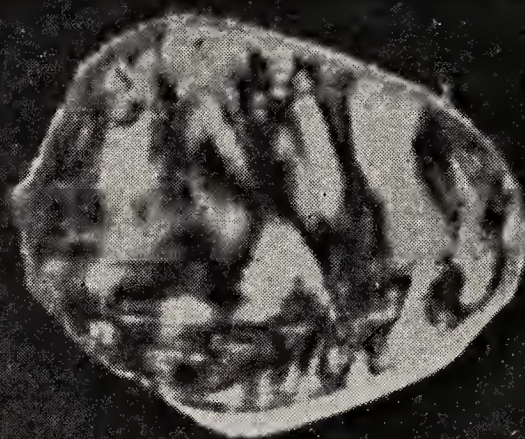
(b) Blue luminescence  
(d) Birefringence



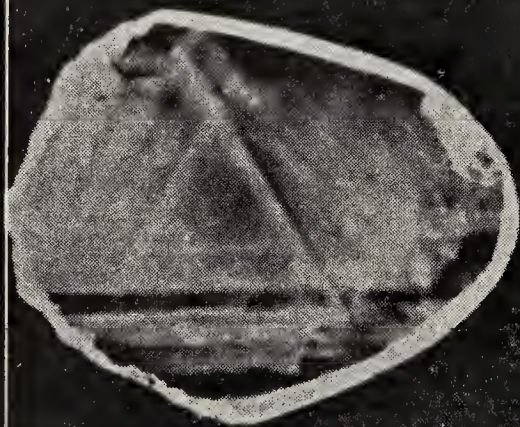
(a.)



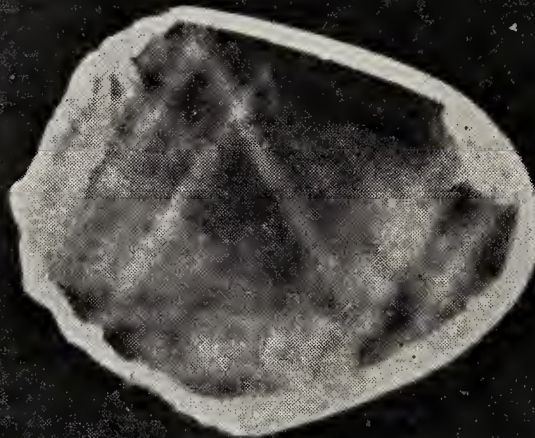
(d)



(b)



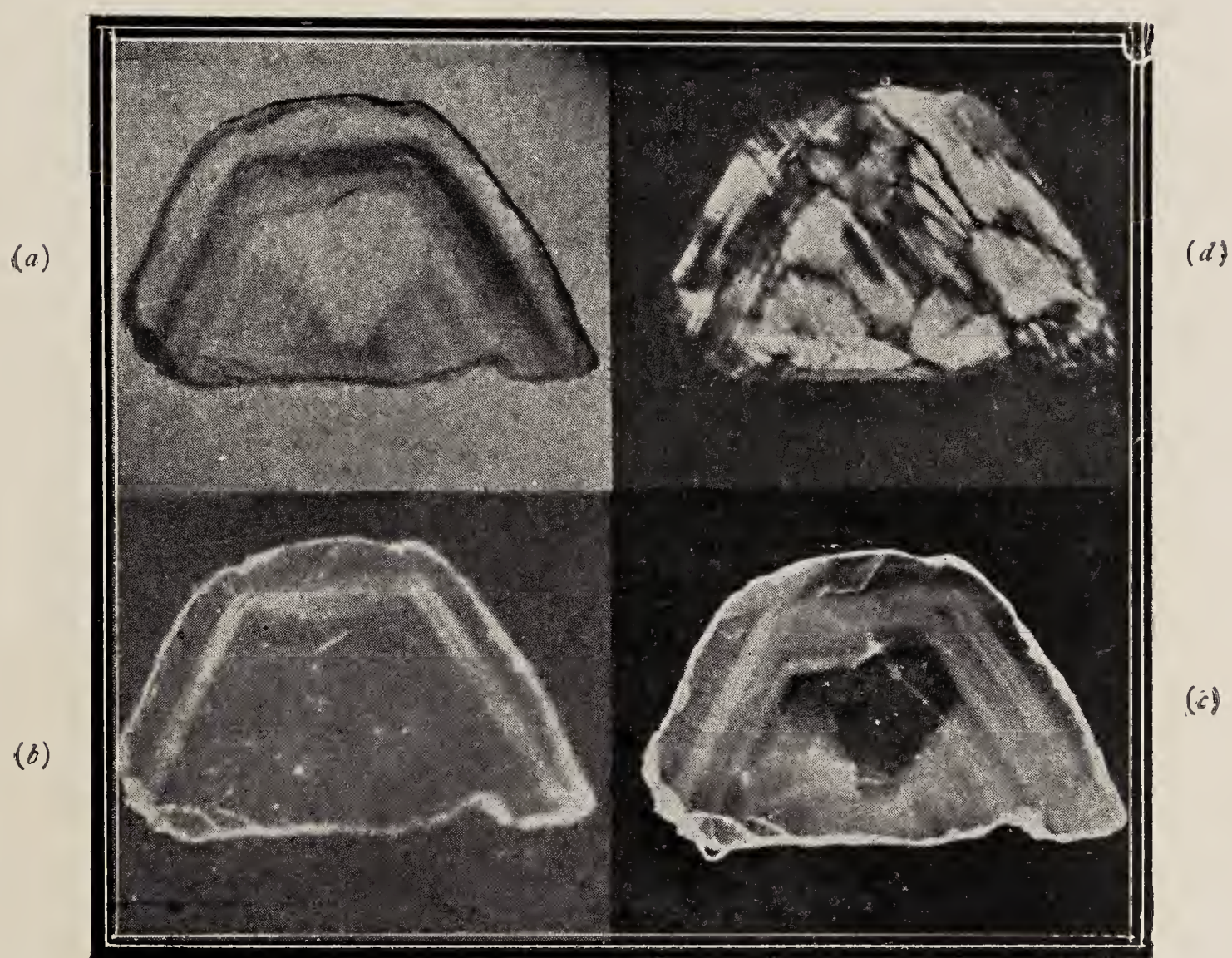
(c)



(a) Ultra-violet transparency  
(c) Yellow luminescence

(b) Blue luminescence  
(d) Birefringence

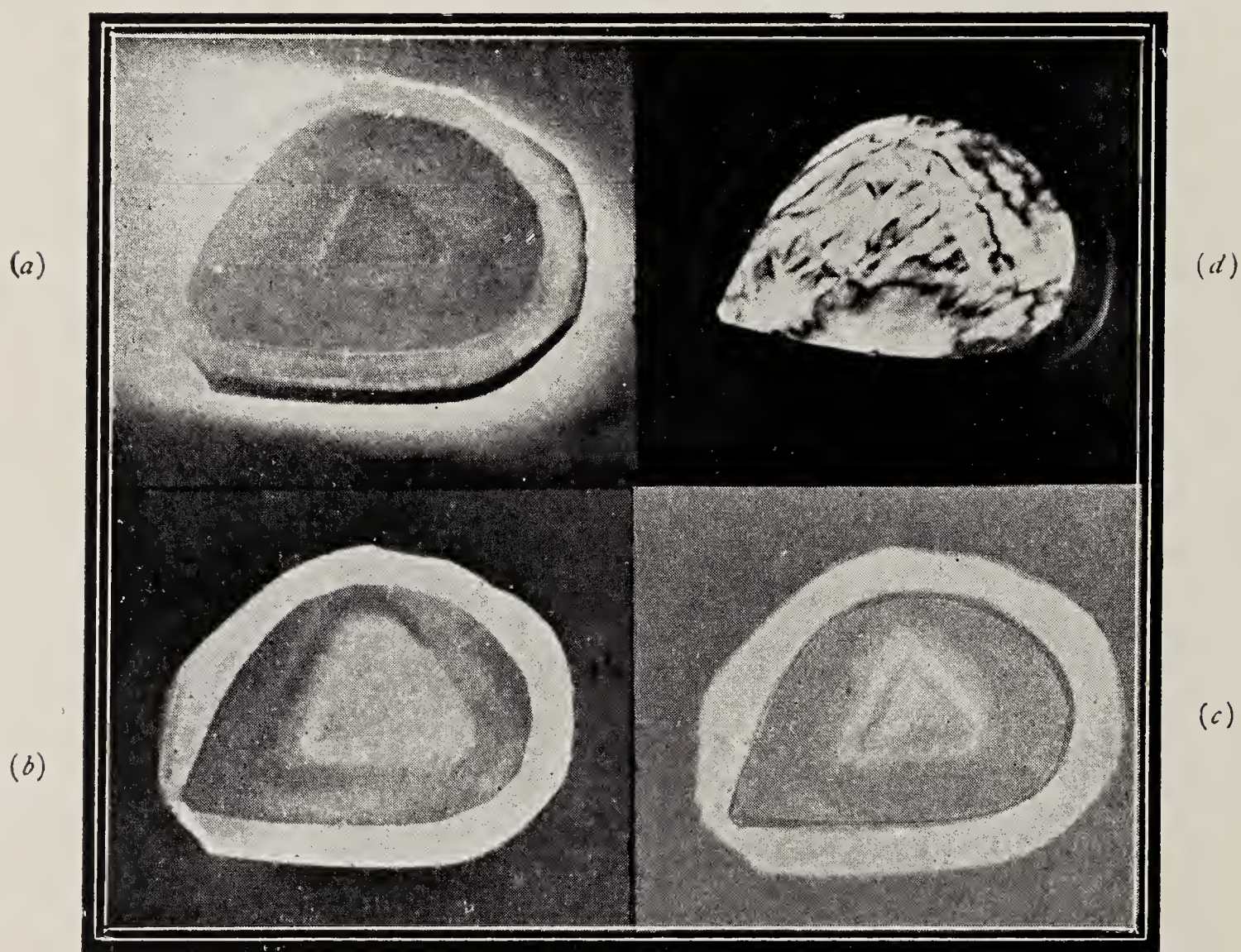




(a) Ultra-violet transparency  
(c) Yellow luminescence

(b) Blue luminescence  
(d) Birefringence

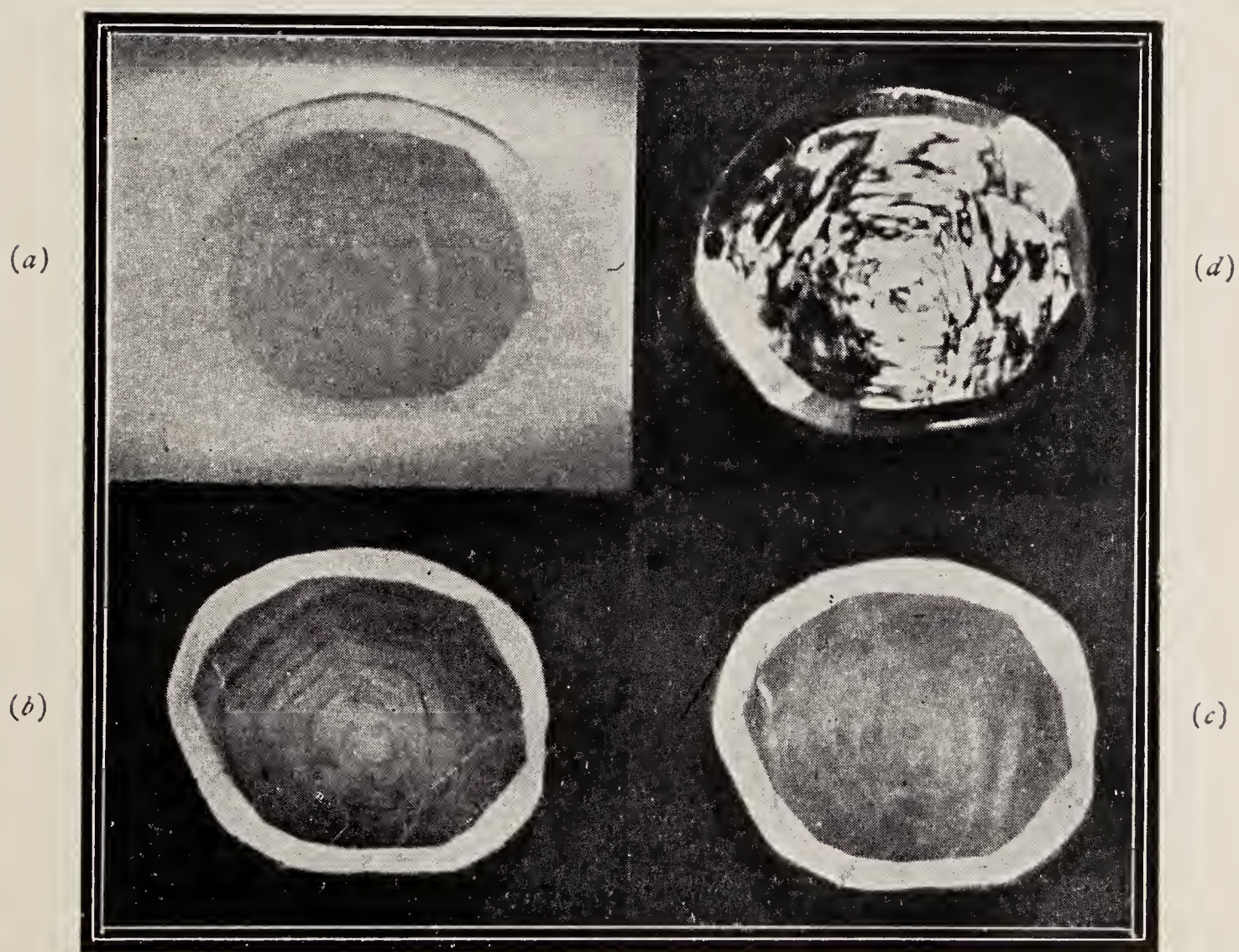




(a) Ultra-violet transparency  
(c) Yellow luminescence

(b) Blue luminescence  
(d) Birefringence





(a) Ultra-violet transparency  
(c) Yellow luminescence

(b) Blue luminescence  
(d) Birefringence







A scrutiny of the photographs reveals other features calling for mention. One of them is the kind of luminescence not exhibited by the perfect diamonds which has been described above as yellow luminescence. The pattern of yellow luminescence is usually, though not always, different from the pattern of blue luminescence. This is evident, for example, on a comparison of figures (b) and (c) in Plate VI, Plate VIII, Plate X and Plate XII. The yellow luminescence often takes the form of a set of parallel bands as for example in Plate VI, Plate VIII, Plate X and Plate XII. Finally, we may draw attention to the fact that the birefringence patterns of the composite diamonds have a configuration not dissimilar to and indeed often resembling closely the other three patterns of the respective diamonds.

We shall now briefly consider what these facts of observation signify. It is well known that diamonds are usually found in nature as complete single crystals which are ordinarily not of any great size. In these circumstances, the composition and properties of any one crystal may be expected to be uniform within its interior. The actual position is rather different, as we have seen. In about ten per cent. of the cases, we find diamond to exhibit a definite set of properties and in another ten per cent. of the cases a different set of properties. Moreover, in a large majority of cases the crystal exhibits regions in its interior where one kind of diamond appears and other regions where the other kind appears. Further, the regions where the two kinds appear are bounded by crystallographic planes of importance, *viz.*, the octahedral or the dodecahedral planes. The only reasonable explanation that can be put forward for this situation is that the crystal structure of diamond may assume one or another of certain alternative forms which are different but nevertheless resemble each other sufficiently to appear in juxtaposition in the same crystal. All the phenomena with which we have been confronted in our studies have to be explained on this basis.

#### 4. SUMMARY

Photographs are reproduced of seven plates of composite diamond exhibiting in each case the variations over its area of the ultra-violet transparency, the blue luminescence, the yellow luminescence and the birefringence. The composite nature of the diamond is also demonstrable by the spectrographic record of its infra-red absorption. The significance of the geometric character of the patterns and of their mutual relationships is discussed.



# THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE

## Part VI. The Free Vibrations of the Structure

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### 1. INTRODUCTION

BEFORE we can usefully take up the discussion of the infra-red activity exhibited by diamond, we have, in the first place, to consider the dynamical behaviour of the structure of the crystal and determine the characteristic modes and frequencies of free vibration of the atomic nuclei which constitute that structure about their positions of equilibrium. The simplicity of the structure and the fact that the atomic nuclei in the crystal all have the same mass makes it possible to deal with this problem and find its solution by an elegant procedure. The basis of the treatment is the theorem in classical mechanics which states that all the possible small vibrations of a connected system of particles are a superposition of a set of normal modes in each of which all the particles oscillate with the same frequency and in the same or opposite phases, the number of the normal modes being the same as the number of dynamical degrees of freedom of movement of the particles in the system. The atomic nuclei being enormously more massive than the electrons, we are justified in considering them as simple mass-particles with the movements of which we are concerned, while the electrons in the crystal are regarded as springs which hold the nuclei in position, the strength of the springs determining the possible frequencies of vibration of the nuclei.

### 2. THE STRUCTURE OF DIAMOND

Diamond exhibits in its structure the most perfect demonstration of the validity of the concept of the tetrahedral carbon atom. Each carbon nucleus is held to four other nuclei grouped around it in an exactly tetrahedral configuration, these four other nuclei again being connected to others grouped around them in the same fashion. The structure thus built up is continued in all directions throughout the volume of the crystal. How and why this tetrahedral configuration is set up and maintained with the perfection actually observed are questions which we shall not here enter into. They will be taken up for consideration later in our discussion of the infra-red



activity of the crystal. What we are here concerned with is the ordering of the atomic nuclei within the volume of the crystal.

The structure of diamond may be described compendiously as composed of two interpenetrating face-centred cubic lattices. For our present purpose, it is more usefully regarded as composed of two interpenetrating rhombohedral lattices, eight nuclei situated at the points of each of which delineate the unit rhombohedral cell. Thus, two sets of eight nuclei, in other words, 16 nuclei taken together form the unit with the dynamical behaviour of which we are concerned in our studies. The nuclei appear in the crystal in equidistant layers parallel to its cubic planes, while in the octahedral layers the nuclei appear in layers which are alternately nearer together and further apart in the ratio of one to three.

### 3. THE NORMAL MODES OF VIBRATION

A crystal is an extended system which is a three-dimensionally periodic array in space of structural units, each of which contains a finite number, which we shall denote by  $p$ , of non-equivalent mass-particles. The interaction of the structural units with each other has, of necessity, to be considered in considering the possible modes of vibration of these structural units. By writing down the equations of motion of the  $p$  non-equivalent particles in any one structural unit and proceeding to solve them to find their normal modes of vibration, it is readily established that there are really eight species of normal modes, all of which are comprised in the following statement: *in any one normal mode, equivalent atoms in the successive cells of the structure situated along its axes have the same amplitude of vibration and a phase which is either the same or else alternates in successive cells of the structure along one, two or all three axes of the lattice.* The alternatives for the three axes of the lattice being independent, we have  $2 \times 2 \times 2$  or 8 distinct possibilities, in other words, 8 distinct species of normal modes. The same result may also be very simply derived from the consideration that the structure of the crystal is brought into coincidence with itself by a unit translation along any one axis, and hence a normal mode of vibration which is a property of the structure must also conform to the principle of translational symmetry. This is possible only if, following a unit translation, the amplitudes of vibration of equivalent atoms remain unaltered and the phases all remain unaltered or else are all reversed. This way of regarding the matter is instructive since it indicates that what we have referred to as the normal modes of vibration of the structural units may equally well be described as the stationary modes of vibration of the extended system of particles forming a periodic structure which constitutes the crystal.



The 8 sets of  $3p$  equations each for the normal modes when solved give us  $24p$  solutions, of which only  $(24p - 3)$  represent actual vibrational modes, the 3 excluded solutions representing the translations of the group of  $8p$  atoms which in effect is the dynamic unit of which the degrees of freedom appear as normal modes. In the case of diamond,  $p = 2$ ; hence we have 45 normal modes of vibration. By reason, however, of the cubic symmetry of the structure, all of these modes are degenerate. A further simplification arises by reason of the fact that the two non-equivalent atoms have the same mass. It turns out that there are only eight distinct and discrete frequencies of free vibration of the structure of diamond corresponding to the modes described and listed below in Table I.

TABLE I

Mode	Description	Degen- eracy	Fre- quency cm. <sup>-1</sup>
I	Oscillation of the two lattices in opposite phases	3	1332
II	Tangential oscillation of the octahedral planes in opposite phases .. ..	8	1273
III	Tangential oscillation of the cubic planes in opposite phases .. ..	6	1219
IV	Normal oscillation of the octahedral planes in opposite phases .. ..	4	1176
V & VI	Normal oscillation of the cubic planes in the same or opposite phases .. ..	3 + 3	1087
VII	Normal oscillations of the octahedral planes in the same phase .. ..	4	1010
VIII	Tangential oscillation of the cubic planes in the same phase .. ..	6	746
IX	Tangential oscillation of the octahedral planes in the same phase .. ..	8	624
	Translations .. ..	3	624→0
	Total ..	48	



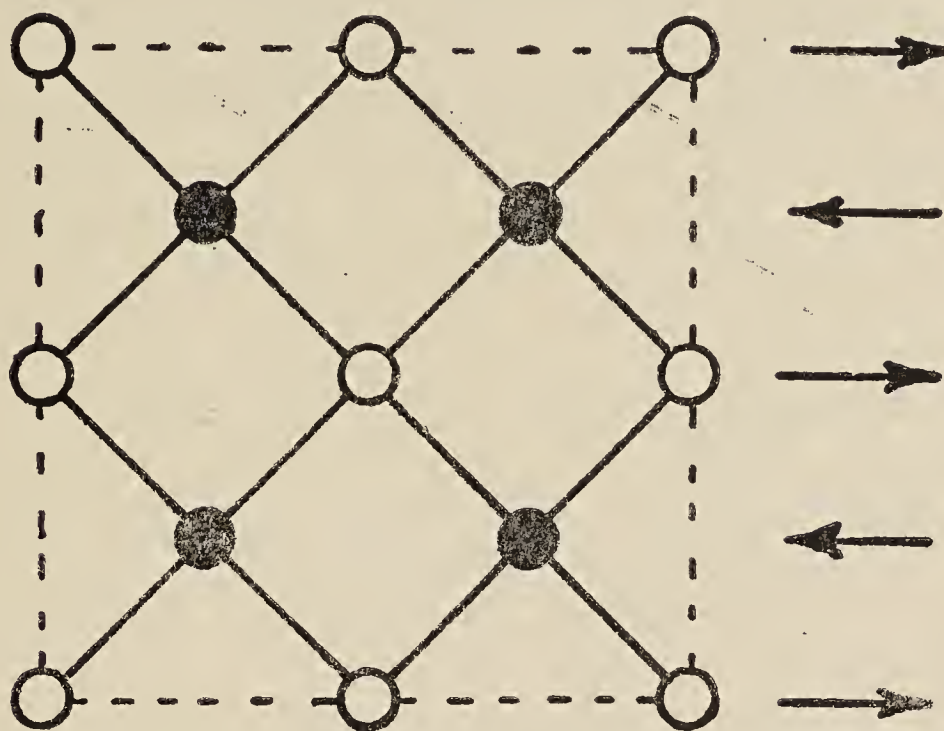


FIG. 1. The triply degenerate mode of highest frequency.

#### 4. DESCRIPTION OF THE NORMAL MODES

The geometric characters of the free vibrations of the structure described and listed in Table I may be deduced in the following manner. Considering a simple rhombohedral lattice, the eight possible situations regarding the phase of the movements at its lattice points give us firstly, a simple translation of the whole lattice, four movements in which the nuclei in the alternate octahedral planes move in opposite phases and three others which are movements of the cubic planes alternately in opposite phases. There are two rhombohedral lattices to be considered and their phases may be either the same or opposed to each other. The directions in which the movements occur are determined by the symmetry of the structure. They would evidently be either normal or tangential to the layers concerned, the tangential movements being twice as numerous as the normal ones. The translations of the two lattices if in opposite phases yield a triply degenerate mode of vibration, and if in the same phase only a simple translation. Thus, in all, we have nine species of normal modes, as shown in Table I with their respective degeneracies, but only eight distinct frequencies since the fifth and sixth modes are indistinguishable.

Figure 1 depicts the triply degenerate mode listed in Table I as that of highest frequency. In Fig. 2, the four octahedral modes are depicted and in Fig. 3, the four cubic modes. In these diagrams, the valence bonds linking the carbon atoms with each other have been shown with a view to indicate the extent to which the movement depicted involves an extension of the valence bonds or changes in the valence-angles. We are thereby enabled to perceive at a glance whether the frequencies of the modes would be high or low and also to compare the different modes with each other,



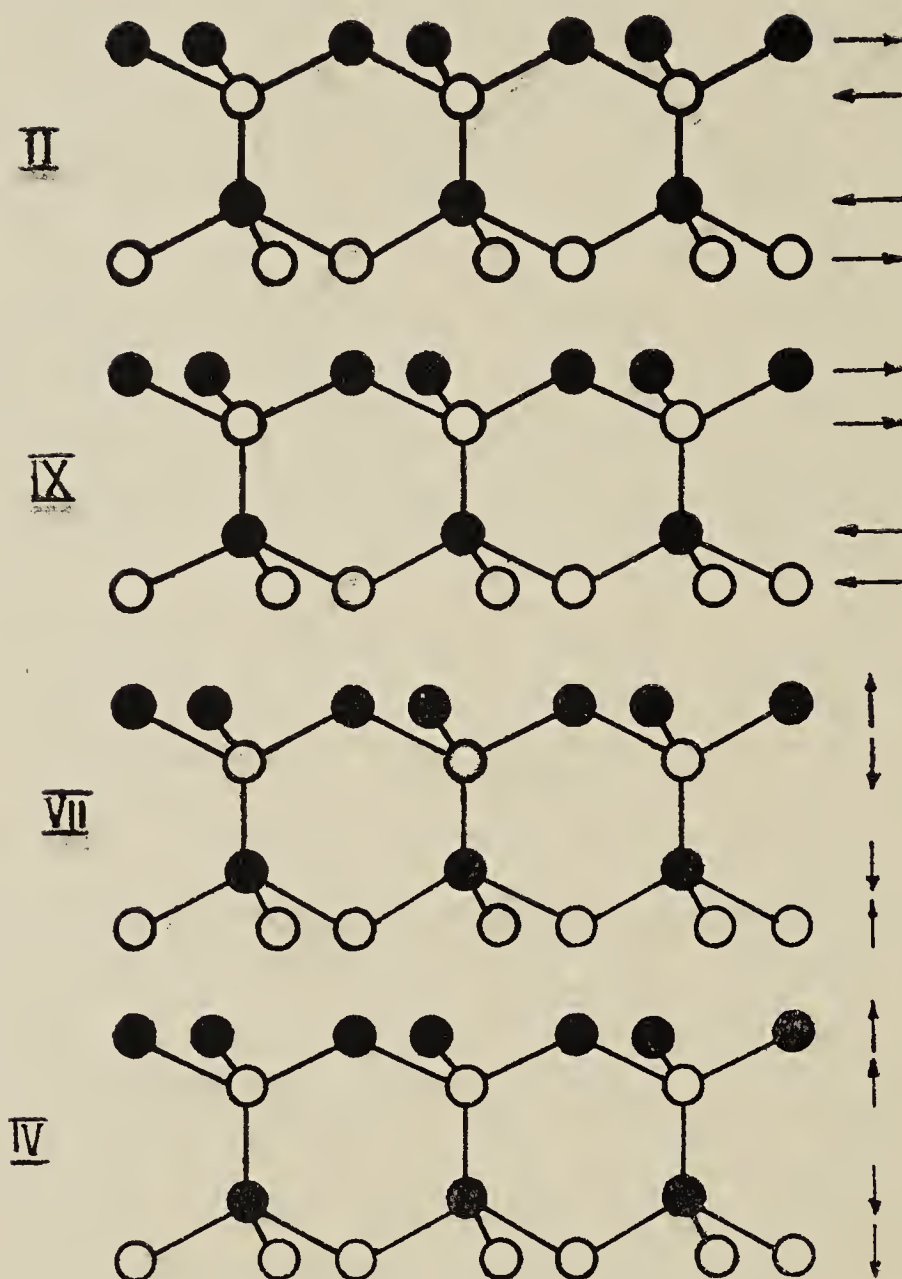


FIG. 2. The four octahedral modes of oscillation.

The mode depicted in Fig. 1 evidently involves a periodic stretching or compression of all the four bonds which connect a carbon with its four immediate neighbours, as also variations of all the bond angles. It follows that this would be the mode of highest frequency. The tangential oscillation in which the adjacent octahedral planes move in opposite phases (marked II in Fig. 2) involves changes in three bond-lengths and would therefore have a high frequency. It appears as mode II in the Table. *Per contra* the mode in which the octahedral planes move in the same phase (marked IX in Fig. 2) does not involve a change in length of any of the four bonds and hence it should have the lowest frequency of all the modes. It is accordingly listed as IX in the Table. The cubic mode marked as VIII in Fig. 3 also involves no changes in bond-lengths and would therefore be of low frequency. It appears as the last entry but one in Table I. The cubic mode marked III in Fig. 3 involves changes in only two bond-lengths out of the four and accordingly takes its place as the third listed in Table I. Modes IV, V, VI and VII take intermediate positions in the list which can only be determined by con-



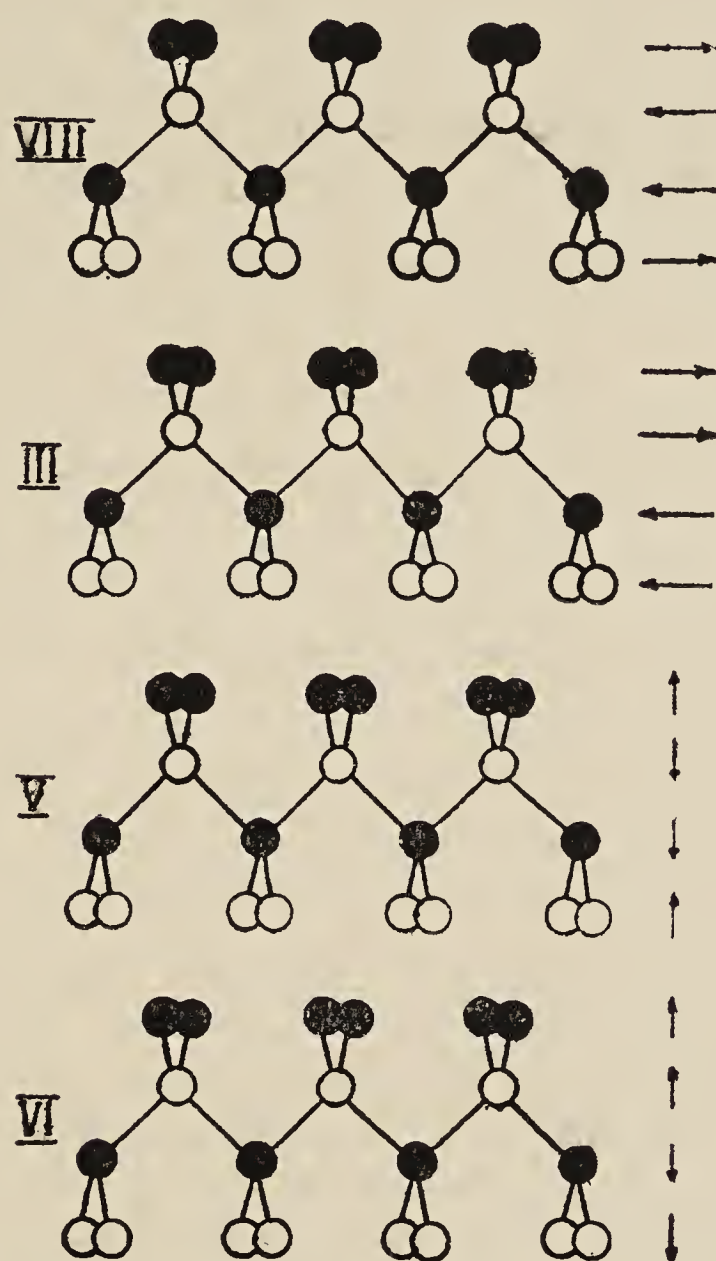


FIG. 3. The four cubic modes of oscillation.

siderations of a quantitative character. These will be set forth in a later part of the memoir.

## 5. SUMMARY

It is shown that the structure of diamond has eight discrete frequencies of free vibration. The mode of highest frequency is an oscillation of the two interpenetrating lattices of carbon nuclei with respect to each other. The other frequencies represent the oscillations of the octahedral or cubic layers in the crystal either normally or tangentially to themselves.



# THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE

## Part VII. The Characteristic Frequencies

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### 1. INTRODUCTION

THE four largest plates of diamond in the author's collection are roughly circular or oval in shape and have a superficial area of about three square centimetres each. Their thickness ranges between 1.1 and 1.5 millimetres. By recording their transmission curves in the range between  $2\mu$  and  $12\mu$  at the very slow speed of 10 minutes per  $\mu$  of wavelength, very satisfactory records have been obtained which are reproduced in the text respectively as Fig. 1, Fig. 2, Fig. 3 and Fig. 4, these being arranged in the order of the increasing thickness of the plate. It should be mentioned that these plates are not perfect diamonds in the sense in which these words were used in the third part of the memoir. For, they exhibit a birefringence pattern. Tests for ultra-violet transparency however indicate that they resemble the perfect diamonds somewhat in their behaviour and this is also evident from their infra-red transmission records. We shall accordingly proceed to find from these records the eight characteristic frequencies of vibration of the structure of diamond, reserving for a later part of this memoir a discussion of the activities of these modes in respect of infra-red absorption of various orders.

As has already been explained in the previous parts of the memoir, the first-order absorption spectrum of diamond makes its appearance at  $7.5\mu$  and extends towards greater wavelengths. Likewise, the second-order absorption commences at  $3.75\mu$  and continues towards the region where the first-order appears. The quantitative relationships between the two orders enable us to recognise and identify the normal modes which give rise to the observed features and to determine their frequencies with considerable precision.

### 2. THE FIRST-ORDER ABSORPTION

The infra-red records leave us in no doubt whatever regarding the vibrational mode of the highest frequency. In Fig. 3, this manifests itself as a



sudden fall of the transmission percentage from 50% at  $7.4\mu$  to complete opacity at  $7.48\mu$  followed by a small rise in transmission to 5% at  $7.5\mu$ , after which it diminishes again. The other figures also indicate that this absorption may be located at  $7.5\mu$ . Expressed in wave-numbers, this is  $1332\text{ cm.}^{-1}$  which is also the frequency derived from studies on the scattering of light by diamond.

The position of the wavelength of the second maximum of absorption is not determinable with the same measure of precision. With thick diamond plates, the curve spreads out as it approaches the line of zero transmission. Hence, the position of this absorption peak is best determined from the records obtained with thinner plates. The mean derived from the records of several diamonds is  $7.85\mu$  or in wave-numbers  $1273\text{ cm.}^{-1}$

Between  $8\mu$  and  $9\mu$ , the records clearly show two other turning points, or maxima of absorption if we so choose to regard them. These may be placed at  $8.2\mu$  and  $8.5\mu$  respectively. In wave-numbers, these are  $1219\text{ cm.}^{-1}$  and  $1176\text{ cm.}^{-1}$  respectively. At greater wavelengths or lower frequencies, the transmission increases rapidly. There is an arrest in such increase between  $9\mu$  and  $9.2\mu$ . At the latter wavelength, it becomes once again very rapid. If we take the dip at  $9.1\mu$  to represent the characteristic wavelength, the characteristic frequency would be  $1098\text{ cm.}^{-1}$ . If, on the other hand, we take  $9.2\mu$  where the curve has its greatest slope as the characteristic wavelength, the characteristic frequency would be  $1087\text{ cm.}^{-1}$ . At still greater wavelengths, the peak of absorption at  $9.9\mu$  is sharply defined and the characteristic frequency can therefore be precisely stated as  $1010\text{ cm.}^{-1}$

### 3. THE SECOND-ORDER ABSORPTION

There is a steep fall in transmission which is very conspicuous in the records and is particularly well shown by Fig. 3 and which commences at  $3.75\mu$ , or in wave-numbers  $2666\text{ cm.}^{-1}$ . This is just double the highest absorption frequency observed in the first order. We can therefore recognise this sudden increase in absorption of the second order as the counterpart of the sudden increase observed in the first order at  $1332\text{ cm.}^{-1}$ . This quantitative relationship demonstrates that the structure of diamond is itself responsible for the absorption spectra of both the first and the second orders.

We have seen that in the first-order absorption the two highest characteristic frequencies of  $1332\text{ cm.}^{-1}$  and  $1273\text{ cm.}^{-1}$  are not fully resolved from each other, the steep rise which indicates the former joining up with the second practically over the whole of its course. Why this is so is a matter which



will be considered later in this memoir. It is mentioned here for the reason if the absorptions due to these normal modes are not separated from each other in the first order, we could scarcely expect that they would be seen clearly separated in the second order. Following the steep increase in absorption which commences at  $3.75\mu$  or  $2666\text{ cm.}^{-1}$ , there is an arrest at  $4\mu$ , and then a diffuse maximum at which we may locate at  $4.1\mu$  or in wave-numbers  $2439\text{ cm.}^{-1}$ . This is exactly double the characteristic frequency of  $1219\text{ cm.}^{-1}$  which we have recognised as the third of the series in the first-order absorption, thereby confirming its determination. The diffuseness of the absorption band having its deepest point at  $4.1\mu$  would be explained by its overlap with the second-order absorption due to the modes of vibration whose frequencies as fundamentals have been located at  $1332\text{ cm.}^{-1}$  and  $1273\text{ cm.}^{-1}$  respectively.

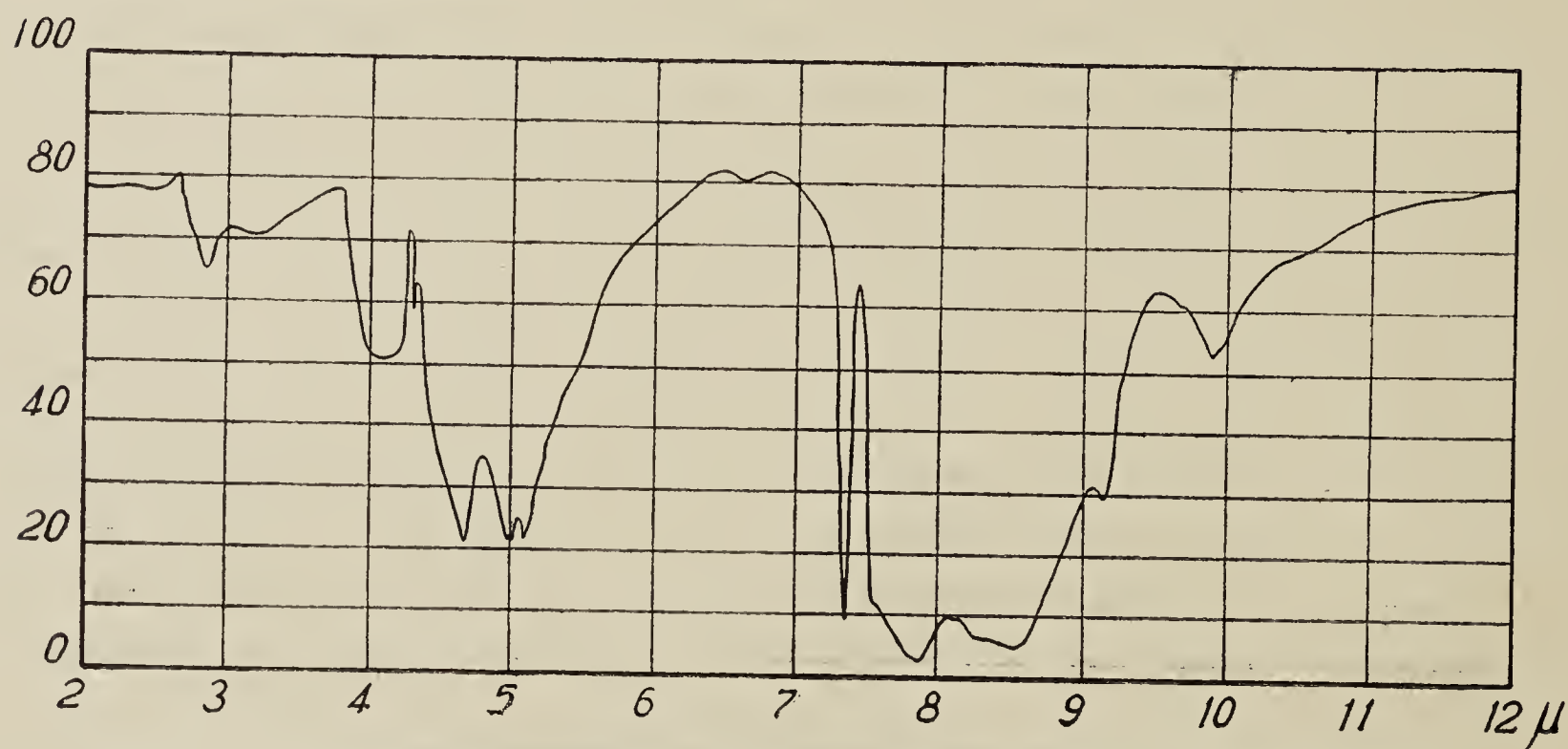


FIG. 1. Percentage Transmission by Diamond; plate thickness 1.19 millimetres.

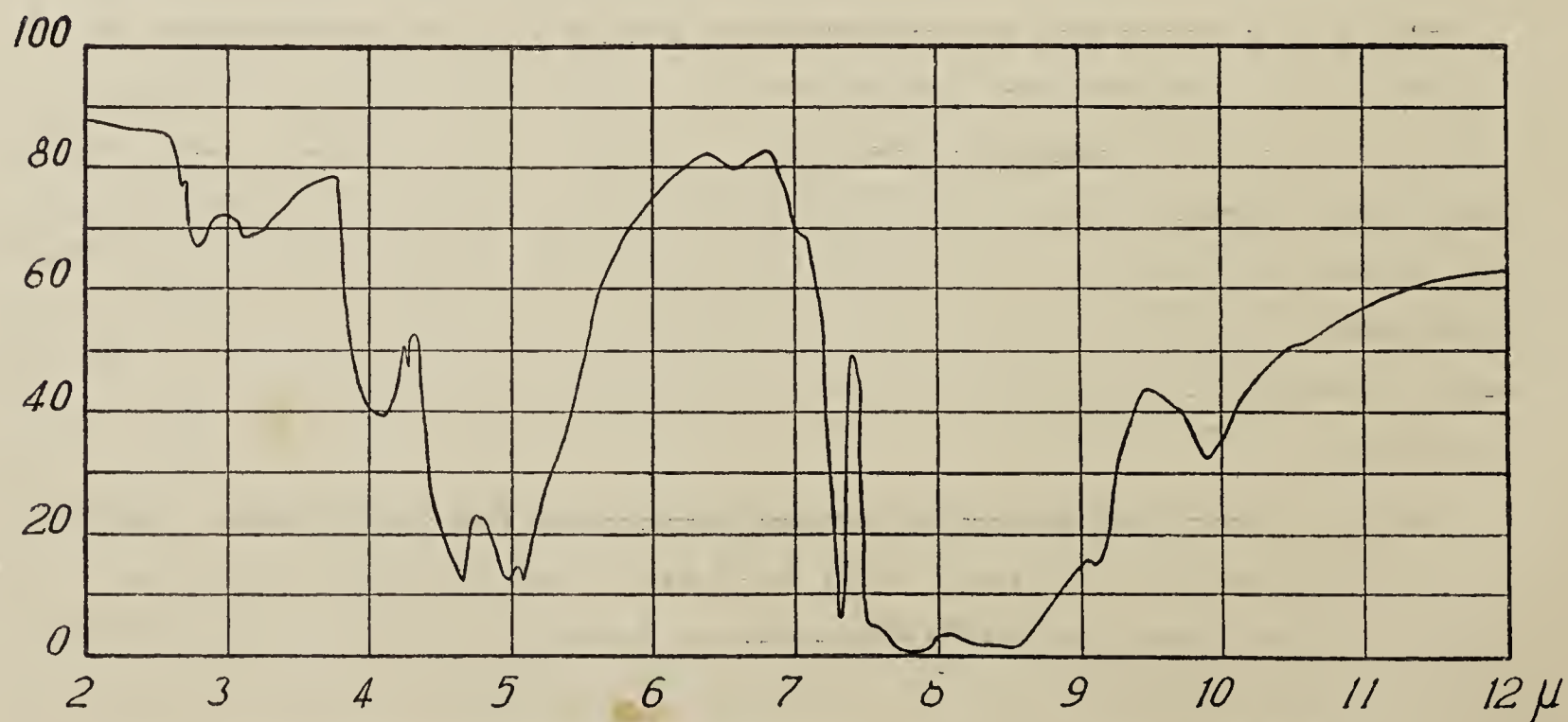


FIG. 2. Percentage Transmission by Diamond; plate thickness 1.40 millimetres.



In all the four figures reproduced with this part of the memoir, a small but clear and sharply defined minimum of transmission appears between the  $4.2\mu$  and  $4.3\mu$  ordinates on the recording sheet. We may locate it as  $4.25\mu$  or  $2352\text{ cm.}^{-1}$ . This is very clearly the octave of the fourth characteristic mode which was located at  $8.5\mu$  or  $1176\text{ cm.}^{-1}$  in the first-order absorption, thus confirming the latter determination.

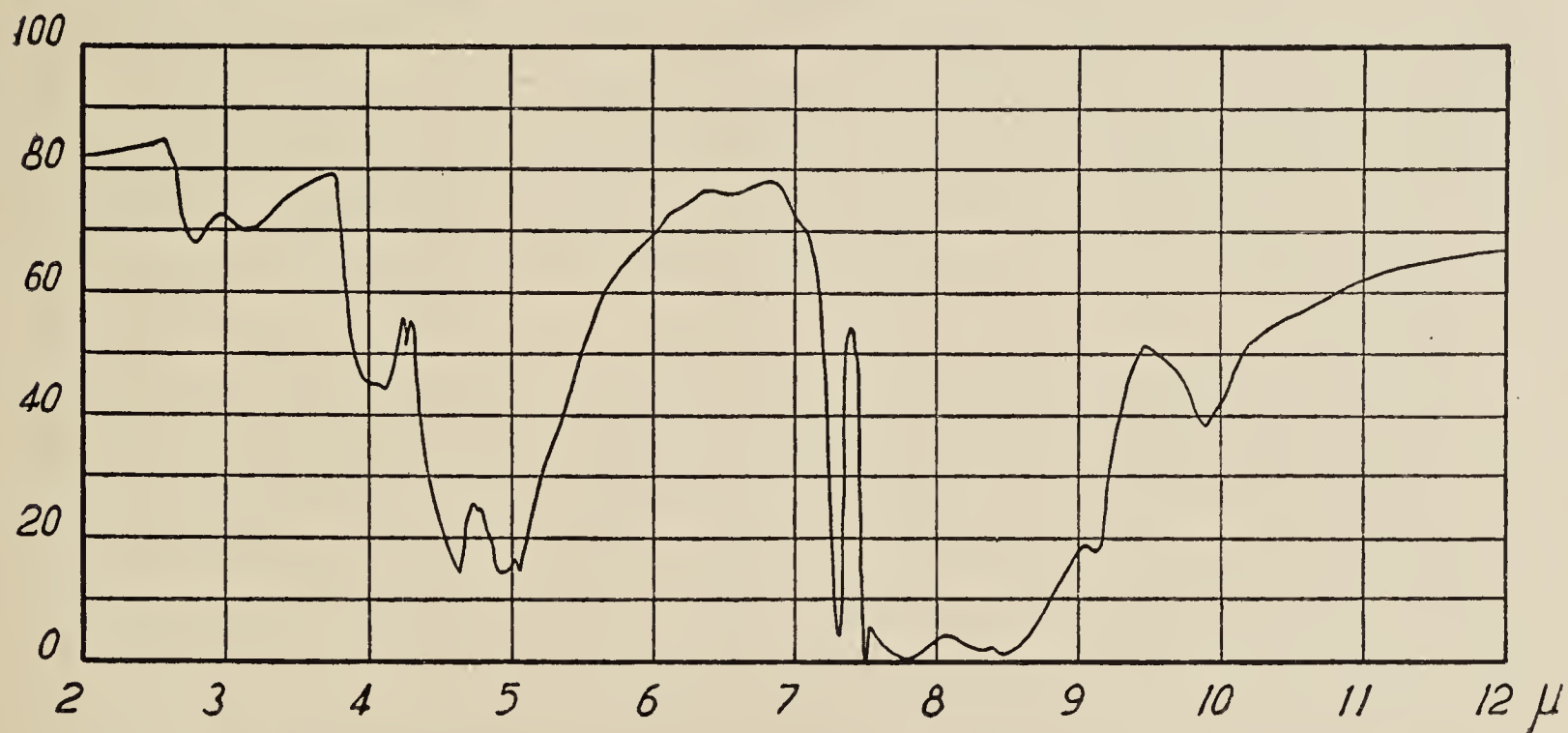


FIG. 3. Percentage Transmission by Diamond; plate thickness 1.44 millimetres.

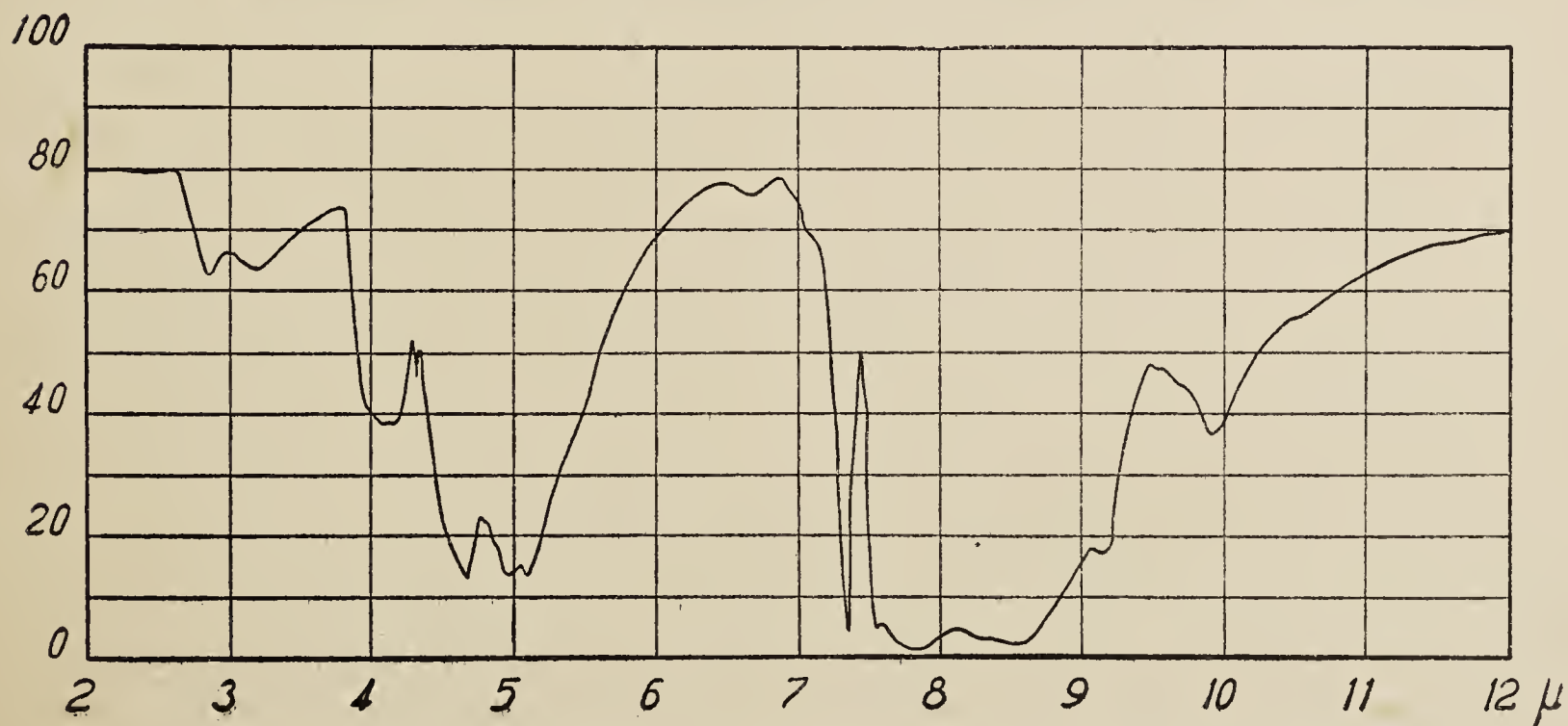


FIG. 4. Percentage Transmission by Diamond; plate thickness 1.49 millimetres.

The sharply defined peak, located at  $4.6\mu$ , is the most striking feature in the records of the absorption spectra of all diamonds. Expressed in wave-numbers, this is  $2173\text{ cm.}^{-1}$ , half of which is  $1087\text{ cm.}^{-1}$  or  $9.2\mu$  when expressed as a wavelength. The wavelength at which the record of the first-order absorption has an inflexion point and exhibits its steepest fall is



also  $9.2\mu$ . We are, therefore, justified in ascribing these features to the same normal mode which is responsible for the extremely pronounced and sharp absorption peak located at  $4.6\mu$  in the second-order absorption. We accordingly recognise  $1087\text{ cm.}^{-1}$  as the fifth characteristic vibration frequency of diamond.

Another feature of the second-order absorption spectrum of diamond, quite as prominent as that considered above, is the minimum of transmission located at  $4.95\mu$ . Expressed in wave-numbers, this is  $2020\text{ cm.}^{-1}$ . This is clearly the octave of the sixth characteristic mode with its wavelength at  $9.9\mu$  or  $1010\text{ cm.}^{-1}$  already recognised in the first-order absorption. The sixth characteristic frequency of diamond of  $1010\text{ cm.}^{-1}$  is thus firmly established.

We may sum up the foregoing by the statement that the first six characteristic frequencies of diamond expressed in wave-numbers are 1332, 1273, 1219, 1176, 1087 and  $1010\text{ cm.}^{-1}$  respectively. They appear as fundamentals in the first-order absorption and with doubled frequencies in the second order, thereby confirming the existence of the respective normal modes and enabling their frequencies to be specified with precision.

#### 4. THE SEVENTH AND EIGHTH NORMAL MODES

In the preceding part of this memoir it was shown that the seventh and eighth normal modes would have frequencies distinctly lower than those of the other six modes by reason of the circumstance that they do not involve any changes in the length of the valence-bonds between the carbon atoms. For the same reason also, their activity in infra-red absorption should be low. Thus, it becomes a question whether any evidence would be forthcoming for the existence of these modes in the records of infra-red absorption.

The manifestation of the first six characteristic frequencies in the transmission curves is accompanied by a rapid decrease in absorption as we proceed from  $7.5\mu$  towards longer wavelengths. Indeed, the absorption at  $12\mu$  is quite small. Hence, if the seventh and eighth characteristic frequencies are lower than  $850\text{ cm.}^{-1}$  it is scarcely to be expected that their presence would be detectable in the first-order absorption spectrum. It is thus in the second-order absorption and not in the first that we should look for evidence of their presence.

Referring to the region between  $6\mu$  and  $7\mu$  in the four spectrographic records reproduced in Figs. 1 to 4 above, one finds in each case a small but quite definite dip in the curve of absorption of a few per cent. which is located



at  $6.7\mu$ , in other words at  $1492\text{ cm.}^{-1}$ . Since all the higher characteristic frequencies appear doubled in the second-order absorption, we may reasonably assume that this dip also represents the seventh characteristic mode appearing in absorption with doubled frequency. Accordingly, we recognise  $746\text{ cm.}^{-1}$  as the seventh fundamental frequency of vibration of diamond.

Recognising  $746\text{ cm.}^{-1}$  as the seventh fundamental, it becomes possible to give an acceptable explanation for other features noticed in the spectrographic records. In the absorption spectra of all diamonds, we find that the peak at  $5\mu$  appears doubled. The major component appearing at  $4.95\mu$  or  $2020\text{ cm.}^{-1}$  has already been recognised above as the double of the sixth characteristic frequency. The other component of the peak located at  $5.09\mu$ , in other words at  $1965\text{ cm.}^{-1}$ , receives a reasonable explanation as a summation of the third and seventh characteristic frequencies ( $1219\text{ cm.}^{-1} + 746\text{ cm.}^{-1} = 1965\text{ cm.}^{-1}$ ). The appearance of this summation is clearly the result of its close approximation in frequency to the octave of the sixth fundamental which is strongly active in the second-order absorption.

Finally, we come to the explanation of the amazingly strong and sharp absorption peak at  $7.3\mu$  noticed in all the four spectrographic records reproduced above. Recognising this absorption located at  $1370\text{ cm.}^{-1}$  as a summation of the seventh and eighth fundamental frequencies, the latter comes out as  $624\text{ cm.}^{-1}$ . The exceptional characters of this absorption are clearly the result of its close approximation in frequency to the fundamental at  $1332\text{ cm.}^{-1}$  which exhibits similarly surprising characters.

## 5. SUMMARY

The absorption spectra of four exceptionally large plates of diamond which were recorded in the NaCl range of the infra-red spectrograph have been critically studied and analysed. From the study it emerges that the structure of diamond has eight characteristic frequencies of free vibration which are respectively 1332, 1273, 1219, 1176, 1087, 1010, 746 and  $624\text{ cm.}^{-1}$ .



# THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE

## Part VIII. Dynamical Theory

BY SIR C. V. RAMAN

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### 1. INTRODUCTION

IN the sixth part of this memoir, it was shown by dynamical reasoning of a very simple and general character that the structure of diamond possesses eight distinct monochromatic frequencies of free vibration. These modes were fully described and exhibited in figures. They were also listed in a table in the descending order of their frequencies in so far as such arrangement could be inferred from the geometry of the modes and its relation to the tetrahedral configuration of the valence-bonds of carbon.

In the foregoing or seventh part of the memoir, the actual values of the eight characteristic frequencies were determined by a study of the spectrographic records of the infra-red absorption by diamond. It is clear, however, that the association of these frequencies with the respective normal modes indicated by the dynamical theory requires further justification. It is necessary, in the first place, to show by further development of the dynamical theory that the normal modes do possess the frequencies actually exhibited in the spectrographic records. It would further be necessary to justify the individual assignments by considering the activity of the respective modes in the absorption of infra-red radiation and comparing it with the facts of observation. Reserving the latter task for the next part of the memoir, we shall proceed to consider the theoretical evaluation of the frequencies of the normal modes.

### 2. THE FIRST APPROXIMATION

The dynamical problem with which we are concerned is very simple. We have only to write down the equations of motion of one single nucleus in the crystal, taking into account its interactions with the surrounding nuclei. The nucleus considered and the interacting nuclei have all the same amplitude and direction of movement, while the phases of movement are all either the



same or opposite. The solution of the equations of motion for the nucleus considered gives the frequency of the normal mode. The different modes differ in their frequencies by reason of the differences in the direction in which the nuclei oscillate in relation to the structure of the crystal, as also by reason of the phases of movement being different. The evaluation of the forces acting on any particular nucleus by reason of its displacements relative to the surrounding nuclei is the essence of the problem. If the resultant of these forces is known, the frequency of vibration can be written down immediately.

The interactions between two nuclei may be defined by considering the components of the relative displacement of the two nuclei and of the force of interaction between them resolved along the cubic axes of the structure and specifying the ratios of the components of force and displacement, otherwise known as the force-constants. The most important internuclear forces are evidently those arising from the displacement of the nucleus under consideration relative to the four nuclei with which it is bonded in a tetrahedral configuration by the valence forces.

The high symmetry of the structure of diamond results in all cases in a very considerable reduction in the number of force-constants appearing in the equations of motion. For instance, only two force-constants are needed to express the interactions with the four nearest neighbours. We may denote them by  $\alpha$  and  $\beta$  respectively;  $\alpha$  refers to the case in which the force and the displacement are both along the same cubic axis, while  $\beta$  refers to the case in which they are mutually perpendicular. The equations of motion in which  $\alpha$  and  $\beta$  and the mass  $m$  of the carbon nucleus appear may be readily written down and solved. As the procedure is very simple, it will be sufficient here to set out the formulæ giving the eight distinct frequencies thus obtained.

Mode I	..	$4\pi^2\nu_1^2c^2m$	$= 4\alpha$
Mode II	..	$4\pi^2\nu_2^2c^2m$	$= (3\alpha + \beta)$
Mode III	..	$4\pi^2\nu_3^2c^2m$	$= (2\alpha + 2\beta)$
Mode IV	..	$4\pi^2\nu_4^2c^2m$	$= (\alpha + 2\beta)$
Modes V and VI		$4\pi^2\nu_{5,6}^2c^2m$	$= 2\alpha$
Mode VII	..	$4\pi^2\nu_7^2c^2m$	$= (3\alpha - 2\beta)$
Mode VIII	..	$4\pi^2\nu_8^2c^2m$	$= (2\alpha - 2\beta)$
Mode IX	..	$4\pi^2\nu_9^2c^2m$	$= (\alpha - \beta)$

The formulæ can be simplified further if the ratio  $\alpha/\beta$  is regarded as known. For example, we may take  $\alpha/\beta$  equal to 2, which is a reasonable



assumption. All the eight frequencies can then be expressed in terms of a single constant. To find this, we may base ourselves on the frequency of mode I which is known to be  $1332 \text{ cm.}^{-1}$  and then proceed to evaluate the other frequencies. We thus obtain the results shown in Table I. The calculated frequencies are all of the right order of magnitude. But they are systematically smaller than the observed values. The reason for this is clearly to be found in our neglect of the interactions of each nucleus with its more distant neighbours.

TABLE I  
*Modes and Frequencies*  
 $\alpha = 3.14 \times 10^5 \text{ dynes/cm.}$   $\beta = 1.57 \times 10^5 \text{ dynes/cm.}$

Modes	Frequency ( $\text{cm.}^{-1}$ ) Calculated	Frequency ( $\text{cm.}^{-1}$ ) Observed
I	1332	1332
II	1246	1273
III	1153	1219
IV	942	1176
V & VI	942	1087
VII	942	1010
VIII	666	746
IX	471	624

### 3. THE SECOND AND THIRD APPROXIMATIONS

The agreement between the calculated and observed frequencies can be improved by taking into account the interactions between the particular nucleus and the twelve other nuclei which are its next nearest neighbours and are all situated at the same distance from it. All these twelve neighbours are located at the points of the same rhombohedral lattice as the nucleus under consideration. They move together with it in mode I and hence in the expression for the frequency of that mode, their interactions do not appear. The position is different with regard to the other modes listed in Table I. In every one of the latter modes, the nuclei in the alternate cubic or octahedral



layers of the structure oscillate in opposite phases and hence the interactions between the nuclei located in the same lattice necessarily appear in the equations of motion. A single additional constant  $\gamma$  suffices to express these interactions, but it appears multiplied by different numerical factors (2 or 4 or 8) for the different modes. The formulæ for the frequencies as thus corrected are given below.

Mode I	..	$4 \pi^2 \nu_1^2 cm$	$= 4a$
Mode II	..	$4 \pi^2 \nu_2^2 cm$	$= 3a + \beta + 2\gamma$
Mode III	..	$4 \pi^2 \nu_3^2 cm$	$= 2a + 2\beta + 4\gamma$
Mode IV	..	$4 \pi^2 \nu_4^2 cm$	$= a + 2\beta + 8\gamma$
Modes V and VI		$4 \pi^2 \nu_{5,6}^2 cm$	$= 2a + 8\gamma$
Mode VII	..	$4 \pi^2 \nu_7^2 cm$	$= 3a - 2\beta + 8\gamma$
Mode VIII	..	$4 \pi^2 \nu_8^2 cm$	$= 2a - 2\beta + 4\gamma$
Mode IX	..	$4 \pi^2 \nu_9^2 cm$	$= a - \beta + 2\gamma$

The interactions of each nucleus with the twelve other still more distant neighbours can be similarly taken care of by introducing still another constant which now appears (multiplied by a numerical factor which may be 1 or 2 or 3 or 4 as the case may be) in all the equations of motion and the formulæ for the frequencies derived therefrom. These formulæ are:

Mode I	..	$4\pi^2 \nu_1^2 c^2 m$	$= 4a + 4\delta$
Mode II	..	$4 \pi^2 \nu_2^2 c^2 m$	$= 3a + \beta + 2\gamma + \delta$
Mode III	..	$4 \pi^2 \nu_3^2 c^2 m$	$= 2a + 2\beta + 4\gamma + 2\delta$
Mode IV	..	$4\pi^2 \nu_4^2 c^2 m$	$= a + 2\beta + 8\gamma + 3\delta$
Modes V and VI		$4\pi^2 \nu_{5,6}^2 c^2 m$	$= 2a + 8\gamma + 2\delta$
Mode VII	..	$4 \pi^2 \nu_7^2 c^2 m$	$= 3a - 2\beta + 8\gamma + \delta$
Mode VIII	..	$4\pi^2 \nu_8^2 c^2 m$	$= 2a - 2\beta + 4\gamma + 2\delta$
Mode IX	..	$4\pi^2 \nu_9^2 c^2 m$	$= a - \beta + 2\gamma + 3\delta$

#### 4. COMPARISON OF THE CALCULATED AND OBSERVED FREQUENCIES

Whereas Table I shows the frequencies calculated on the basis of a single constant, Table II exhibits the results of the calculation with three constants



TABLE II

*Modes and Frequencies*

$\alpha = 3.14 \times 10^5$  dynes/cm. ;  $\beta = 1.64 \times 10^5$  dynes/cm. and  $\gamma = 0.26 \times 10^5$  dynes/cm.

Modes	Frequency (cm. <sup>-1</sup> ) Calculated	Frequency (cm. <sup>-1</sup> ) Observed
I	1332	1332
II	1279	1273
III	1224	1219
IV	1096	1176
V & VI	1087	1087
VII	1077	1010
VIII	746	746
IX	534	624

TABLE III

*Modes and Frequencies*

$\alpha = 2.78 \times 10^5$ ;  $\beta = 1.75 \times 10^5$ ;  $\gamma = 0.25 \times 10^5$ ;  $\delta = 0.36 \times 10^5$  dynes/cm.

Modes	Frequency (cm. <sup>-1</sup> ) Calculated	Frequency (cm. <sup>-1</sup> ) Observed
I	1332	1332
II	1244	1273
III	1233	1219
IV	1150	1176
V & VI	1081	1087
VII	1008	1010
VIII	731	746
IX	607	624



and Table III with four. The values of  $\alpha$  used are the same in Tables I and II and also the same as the value of  $(\alpha + \delta)$  in Table III. The constants  $\beta$  and  $\gamma$  used in the three tables are also not very different. Hence, the improved agreement which is apparent between the calculated and observed frequencies is very clearly the result of taking the interactions with 4, 16 and 28 neighbours into account respectively in the three cases. It is worthy of special remark that whereas the calculated frequencies of modes IV, V, VI and VII are all the same in Table I, they show a small progressive fall in Table II, but only in Table III do they actually fall into line with the observed frequencies.

We are thus fully justified in inferring from the results of these calculations that the characteristic frequencies determined by a study of the spectroscopic records are actually the frequencies of the normal modes of vibration of the structure of diamond deduced from the dynamical theory.

## 5. SUMMARY

The eight characteristic frequencies of vibration of the structure of diamond are theoretically evaluated in the first, second and third approximations, taking successively into account the interactions of each nucleus with its 4, 16 and 28 neighbours. A satisfactory agreement emerges between the calculated frequencies and those observed spectroscopically.



# THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE

## Part IX. The Activity of the Normal Modes

BY SIR C. V. RAMAN

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### 1. INTRODUCTION

IN the preceding parts of this memoir, the infra-red behaviour of diamond in its relation to other observable properties has been fully set out, and the free vibrations of its structure have also been adequately discussed. We now proceed to consider the explanation of the one in terms of the other. Various questions here arise which need an answer. Why is there any absorption of infra-red radiation in its passage through diamond? What part do the nuclei and the electrons in its structure respectively play in this phenomenon? Why do some diamonds exhibit infra-red absorption both of the first order and of the second order, and why do others exhibit only the second-order absorption? Why do the different normal modes exhibit very different infra-red activities and why do such activities differ respectively in the first-order and second-order absorption? What is the explanation of the relationships actually observed between the infra-red behaviour of diamond and such other properties as ultra-violet transparency and luminescence? It will be our purpose in the present part of the memoir to return answers to these questions.

### 2. THE MECHANISM OF INFRA-RED ABSORPTION

The absorption of infra-red radiation in its passage through a crystal involves the conversion of the energy of the electromagnetic field into vibrational energy in the solid, in other words, its degradation into heat. The spectrographic records show that the absorption is preferential with respect to certain modes or frequencies of vibration. We naturally, therefore, turn our attention first to the movements of the atomic nuclei in the crystal and consider the action of the electric field of the incident radiation on the positive charges of these massive particles. Here, however, we find in all the normal



modes of vibration, that for every nucleus which is in oscillation, there is another nucleus which is a near neighbour and oscillates with the same amplitude but in an opposite phase. Hence, considering them together, the net transference of energy from the field to the nuclei would be a vanishing quantity. In other words, the atomic nuclei do not play the primary role in infra-red absorption, and we have to recognise the electrons or negative charges in the crystal as the active agents in that process. The field of the radiation disturbs the electrons and their movements result in the nuclei being disturbed from their positions of equilibrium and set into vibration. But it is the electronic movements associated with such vibrations and not the movements of the nuclei themselves which react with the field and result in the absorption of the incident radiation.

From what has been stated, it follows that in seeking for an explanation of infra-red activity, we have to fix our attention on the movements of the electronic charge-clouds in the crystal. It is the symmetry of the distribution of the negative electric charge in its undisturbed state as well as when it is modified by the nuclear movements which determines the appearance or non-appearance of infra-red absorption and its actual magnitude when observed.

### 3. THE SECOND-ORDER ABSORPTION SPECTRUM

Since all diamonds exhibit the absorption spectrum of the second order, it is appropriate that we first consider how such absorption arises. We may, for the present, leave out of consideration the mode of highest frequency and discuss the infra-red activity of the other modes of vibration of lower frequencies. It is a specific feature of all these modes that the alternate layers of nuclei located at the points of the same lattice oscillate in opposite phases. Hence the electrons attached to the nuclei in those layers would also oscillate in opposite phases. Hence, it might be thought that the displacements of electric charge when summed up would vanish and hence that these vibrational modes would fail to exhibit any infra-red activity. But this conclusion is subject to an important qualification, *viz.*, the movements considered are of infinitesimally small amplitude. When this is no longer the case, the approach of any two layers towards each other and the recession of the next two layers from each other would not necessarily produce equal displacements of electric charge. Their difference would represent the resultant displacement of charge and this would evidently be periodic with *twice the frequency* of the vibrational mode. It follows that there could, in favourable circumstances, be an absorption of radiation having *double*



*the frequency* of each of the vibrational modes under consideration. This, to put it briefly, is the explanation of the absorption spectrum of the second order exhibited by all diamonds.

Infra-red activity of the second order demands that the normal mode under reference should result in the negative charges suffering displacements of substantial magnitude. Whether this is actually the case would depend upon the nature of the vibration. When we compare the different normal modes with each other from this point of view, it becomes evident that their infra-red activity would be very different in the different cases. Indeed, we could without difficulty group the modes in the order of the strength of the infra-red activity which they might be expected to display.

Consider, for example, modes VIII and IX which have the two lowest frequencies, *viz.*, 746 and 624  $\text{cm}^{-1}$  respectively. These movements are tangential respectively to the cubic and the octahedral layers and do not involve any changes in the lengths of the valence bonds between the carbon atoms. In these circumstances, it is not to be expected that they would result in any substantial displacements of electric charge. In mode IX, the layers which move laterally with respect to each other are farthest removed, while the layers which are closer move together. Hence, this mode could exhibit no observable activity. Mode VIII is a slightly different case, since the oscillating layers are not so far apart. Hence it might exhibit a very feeble infra-red activity of the second order.

In striking contrast with the two modes of the lowest frequency are modes V and VI which have a common frequency of 1087  $\text{cm}^{-1}$ , and mode VII which has a frequency of 1010  $\text{cm}^{-1}$ . Modes V and VI are oscillations of the cubic layers, while mode VII is an oscillation of the octahedral layers, in both cases in directions normal to themselves. These modes involve changes in the lengths of the valence bonds as well as changes in the bond angles and adjacent atomic layers alternately approach and recede from each other along their common normal. Hence we should expect these modes to exhibit infra-red activity of the second order in a high degree.

Mode IV which has a frequency of 1176  $\text{cm}^{-1}$  stands in a category by itself. It resembles mode VII in being an oscillation of the octahedral layers normal to themselves, but differs from it by reason of the fact that the layers which are close to each other move together and only the layers which are farthest apart alternately approach and recede from each other. In consequence, only one bond length out of the four changes its length periodically and all the bond angles remain unaltered. In these circumstances, we may



indeed expect displacements of charge which would give rise to absorption of the second order, but they would necessarily be very much smaller than in the case of the modes V, VI or VII.

Finally, we may consider modes II and III whose frequencies are respectively  $1273 \text{ cm.}^{-1}$  and  $1219 \text{ cm.}^{-1}$ . These are tangential oscillations of the octahedral and cubic layers respectively, but they involve changes of bond lengths as well as of bond angles. It follows that these modes would give rise to substantial displacements of electric charge. But their infra-red activity would necessarily be weaker than those of the modes VI and VII where the movements are normal to the layers concerned.

The foregoing remarks may be regarded as an interpretation or elucidation of the actually observed features of the second-order spectrum of diamond described and illustrated in the seventh part of this memoir.

#### 4. INFRA-RED ACTIVITY OF THE FIRST ORDER

We shall now proceed to consider the activity of the principal mode of vibration having the highest frequency which is manifested by the perfect diamonds. Expressed in wave-numbers, this frequency is shown by studies on the scattering of light to be  $1332 \text{ cm.}^{-1}$ . This is also the value exhibited in the first-order absorption spectrum. The feature which distinguishes this mode from the several others of lower frequencies is that the vibrations appear in the same phase in the successive cells of the structure along its axes and not alternately in opposite phases as in these other modes. As a consequence, the effects arising from the individual cells of the structure are coherent and cumulative and the observable result attains large values. We may illustrate this remark by reference to the case of magnesium oxide which has been thoroughly investigated and reported on by the author in a recent publication. MgO has a cubic structure resulting from the interpenetration of two rhombohedral lattices occupied by Mg and O respectively. The highest fundamental frequency of vibration of the MgO structure is  $490 \text{ cm.}^{-1}$ . The absorbing power at the corresponding wavelength of  $20.4 \mu$  is so extremely large that radiations of that wavelength incident on the crystal are totally reflected. To exhibit the absorption spectrum of MgO in the wavelength region between  $15 \mu$  and  $24 \mu$ , it is found necessary to use specially prepared films in which the absorption path does not exceed  $3 \mu$ . On the other hand, the second-order absorption spectrum of MgO appearing in the wavelength region between  $10 \mu$  and  $15 \mu$  is readily recorded with plates whose thickness may be as great as one millimetre. It is evident from this that the first-order absorption of MgO is enormously more powerful than the absorption of the second-order.



Diamond, on the other hand, does not exhibit any enhanced reflecting power in the region of wavelengths between  $7.5\mu$  and  $10\mu$ , and the fact that we can use plate thicknesses of a millimetre or more in studying its absorption spectrum in this range of wavelengths is a clear indication that the first-order absorption is extremely weak. That it is, however, not a spurious effect due to defects of structure or extraneous impurities is made abundantly clear by the facts set forth earlier in this memoir. In particular, it should be mentioned that though the first-order is weak, it is not weaker than the second-order absorption. The constancy of the relative strength of the first and second-order absorption spectra in numerous specimens of perfect diamond, and the fact that the same vibrational modes which are manifested in the first order appear with doubled frequencies in the second order, is a clear indication that the first-order absorption exhibited by the perfect diamonds is a fundamental property of such diamonds.

The case of MgO mentioned above serves as a useful pointer in other respects as well. The powerful infra-red activity of the first order which MgO exhibits is a consequence of the two interpenetrating lattices in its structure carrying atoms which are different. In the case of diamond, on the other hand, the nuclei located at the points of the two interpenetrating lattices are identical. But, as has already been remarked, what we are here concerned with are the symmetry properties of the distribution of negative electric charge in the crystal. As the two lattices are constituted of nuclei carrying the same positive charge, any suggestion that one of the lattices carries a larger share of the electronic charge-cloud than the other can be ruled out immediately. Not only is such a situation inherently improbable, but it would also have consequences which are disproved by the facts of the case. Any lack of symmetry in the density of the charge distribution as between the two lattices would result in an enormously more powerful first-order absorption than that actually observed. All that we can legitimately infer from the observed infra-red behaviour is that in the structure of the diamonds which exhibit the first-order absorption, the electronic configuration, meaning thereby the variables which specify the state of the electrons in the crystal, including especially the orientations of their spins, do not conform to the requirements of octahedral symmetry, whereas in the diamonds in which the first-order absorption is absent, these requirements are satisfied.

The foregoing may be summed up by the statement that the electronic states in perfect diamonds possess only the lower or tetrahedral symmetry of the cubic class, while in the non-luminescent class of diamond they have the higher or octahedral symmetry. The situation here recognised enables



us to understand the very significant relationship which is observed between the spectroscopic behaviour of diamond in regions of the spectrum which are so far apart as the infra-red between  $7\mu$  and  $12\mu$  and the ultra-violet between  $0.2\mu$  and  $0.3\mu$ . If the differences in infra-red behaviour are ascribable to differences in the electronic configuration, corresponding differences are necessarily expected in the ultra-violet absorption spectra. It also becomes intelligible why the diamonds of group A and group B exhibit contrasting behaviours in respect of luminescence. Absorption of the incident radiation is a *sine qua non* for its re-emission in a modified form which is termed luminescence. Whereas diamonds of group A do absorb radiation in the near ultra-violet, group B diamonds are transparent to such radiations. It is, therefore, not surprising that group A diamonds exhibit luminescence whereas group B diamonds do not.

It may also be remarked that the inference from the infra-red data that group A diamonds possess only tetrahedral symmetry of the electronic configuration whereas group B diamonds exhibit the full octahedral symmetry receives massive support from the well-established facts regarding the crystal morphology of diamond, as well as from the phenomena of X-ray diffraction in diamond. But it would take us too far from our present theme to enter into these matters in detail. We therefore now return to a discussion of the details of the first-order absorption spectrum.

## 5. CHARACTERS OF THE FIRST-ORDER SPECTRUM

As has been amply illustrated by the spectrographic records reproduced in the earlier parts of this memoir, one of the remarkable features of the first-order absorption is the sudden change from a high degree of transparency to complete or nearly complete opacity occurring at the characteristic frequency of  $1332\text{ cm.}^{-1}$  or wavelength  $7.5\mu$ . At lower frequencies or longer wavelengths, the absorption shows a progressive diminution and ceases to be significant beyond  $12\mu$ . The curve of the percentage transmission between these wavelengths represents the effect of the movements of the electronic charge-clouds in the crystal excited by the incident radiation. The changes in its course at various points indicate the influence of the nuclear vibrations of lower frequencies. The activity of these modes in the first-order absorption rapidly decreases as the difference between their frequencies and the frequency of the active fundamental of highest frequency increases. This indicates that the electronic linkages in the crystal result in a coupling between the various possible modes of vibration of the nuclei. A striking illustration of such coupling is furnished by the astonishing intensity and sharpness of the absorption peak at  $7.3\mu$  or  $1370\text{ cm.}^{-1}$ , which appears sepa-



rated in the records from the steep increase in absorption at  $7.5\mu$  or  $1332\text{ cm.}^{-1}$ . The absorption at  $1370\text{ cm.}^{-1}$  is clearly the result of the summation of the two lowest frequencies ( $746\text{ cm.}^{-1} + 624\text{ cm.}^{-1}$ ) of the diamond structure. That it shows up in such a remarkable fashion is a consequence of its close approximation in frequency to the major absorption at  $1332\text{ cm.}^{-1}$ . It is also an impressive demonstration that the vibrational modes which manifest themselves in the infra-red absorption of diamond have sharply-defined monochromatic frequencies.

## 6. SUMMARY

The features appearing in the second-order absorption of diamond are discussed and explained in terms of the periodic variations with doubled frequency of the electronic charge-density resulting from the nuclear vibrations. The origin of the first-order absorption spectrum exhibited by the perfect diamonds is also discussed. The observed facts indicate that the electronic states in these diamonds possess only tetrahedral symmetry, while in the diamonds which do not show the first-order absorption exhibit the full octahedral symmetry.



# THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE

## Part X. Evaluation of the Specific Heat

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### 1. INTRODUCTION

EINSTEIN in his classic paper of 1907 introducing the quantum theory of specific heats showed that the thermal energy content of all material bodies depends in a fundamental way on the vibration frequencies of their atomic constituents in the region of the infra-red. Crystalline solids were included within the scope of his theory and the case of diamond was specially considered by him in the paper. The very striking changes which appear in the specific heat of diamond with alterations in temperature had been discovered by H. F. Weber in the year 1875 and Einstein made use of Weber's data to illustrate and support his theory. Assuming that the atoms in diamond had a single characteristic frequency of vibration corresponding to an infra-red wavelength of  $11\ \mu$ , Einstein showed that the general trend of the specific heat changes observed by Weber could be accounted for.

In the preceding parts of this memoir, it has been shown that the structure of diamond has eight specific frequencies of free vibration lying in the wavelength range between  $7.5\ \mu$  and  $16\ \mu$ . The spectrographic record of infra-red absorption by diamond enables us to recognise these frequencies and determine them with the necessary precision. It is, therefore, appropriate that we devote the concluding part of this memoir to showing that on the basis of the spectroscopically determined frequencies, and without introducing any other data or any arbitrary constants, the entire course of the variation of the specific heat of diamond over the temperature range from the absolute zero upwards to  $1000^\circ\text{K}$ . can be computed. A comparison will also be made of the results of the computation with the latest available data on the thermal energy content of diamond.

### 2. THE THEORY OF EINSTEIN

We may usefully here sketch the theory of the specific heats of crystals as envisaged by Einstein. He begins by showing that the acceptance of Planck's



radiation formula leads to the consequence that the energy of a resonator capable of absorbing or emitting radiation with a specific frequency could only increase or diminish by quanta proportional to that frequency. A procedure which enables this principle to be used for the evaluation of the thermal energy of crystals is then outlined. The thermal energy is identified with the mechanical energy of vibration of an immense number of *individual* oscillators distributed over the volume of the crystal. The total number of these oscillators is assumed to be the same as thrice the number of atoms comprised in the crystal. It is further assumed that the oscillators can be grouped into sets, each set comprising a great number of individual oscillators characterised by a common frequency of vibration. The individual oscillators in each set occupy the various energy levels allowed by the quantum hypothesis for the particular frequency. The numbers occupying these levels are in the relative proportions determined by the respective energies and by the temperature as indicated by the principle of Boltzmann. The average energy of an oscillator in each of the sets is then evaluated. Summing up over all the oscillators in each of the sets, and then over all the sets, Einstein obtained an explicit formula for the thermal energy of the crystal as a function of the temperature.

It is evident that there is adequate justification for the various steps in the foregoing argument. A crystal is an assembly of a great number of similar and similarly situated groups of atoms, the modes and frequencies of vibration of which would necessarily all be identical. The total number of degrees of dynamical freedom of the entire system may therefore be divided up into sets, each set representing a great number of individual oscillators having a common frequency. Since these oscillators are interconnected, they can exchange energy with each other and thereby constitute a system in thermodynamic equilibrium of which the behaviour could be statistically described in terms of Boltzmann's principle. The argument implies that the atomic vibration spectrum of a crystal would exhibit a set of frequencies, their number being the same as the number of sets of oscillators which are the carriers of the thermal energy. By virtue of Boltzmann's principle, the distribution of this energy over the volume of the crystal would exhibit fluctuations both in space and in time, the magnitude of the fluctuations being the greater, the higher the frequency of the oscillators under consideration.

### 3. THE SPECTRUM OF FREE VIBRATIONS

The modes of free vibration of the structure of diamond were determined and described in the sixth part of this memoir. In the subsequent parts of this memoir, the characteristic frequencies of vibration as found from the



spectroscopic records were assigned to their respective modes on the basis of a theoretical evaluation of the frequencies and confirmed by a comparison of the activities theoretically to be expected with the activities actually found. We are thus on firm ground in listing the modes, their frequencies and their respective degeneracies as shown in Table I and making the entries in the Table the basis for the evaluation of the thermal energy of diamond as a function of the temperature.

TABLE I  
*Modes, degeneracies and frequencies*

Mode	Description	Degeneracy	Frequency cm. <sup>-1</sup>
I	Oscillation of the two lattices in opposite phases .. .. .	3	1332
II	Oscillation of the octahedral layers tangentially in opposite phases .. .. .	8	1273
III	Oscillation of the cubic layers tangentially in opposite phases .. .. .	6	1219
IV	Oscillation of the octahedral layers normally in the same phase .. .. .	4	1176
V & VI	Oscillation of the cubic layers normally in the same or opposite phases .. .. .	3 + 3	1087
VII	Oscillation of the octahedral layers normally in opposite phases .. .. .	4	1010
VIII	Oscillation of the cubic layers tangentially in the same phase .. .. .	6	746
IX	Oscillation of the octahedral layers tangentially in the same phase .. .. .	8	624
	Translations .. .. .	3	624→C
	Total ..	48	..

The 48 degrees of freedom represented in Table I are the degrees of freedom of movement of the 16-atom group which is the dynamic unit in the structure of diamond, *viz.*, two groups of eight atoms each located respectively at the corners of the unit cells of two interpenetrating rhombohedral



lattices. All except three of these degrees of freedom are represented by discrete modes and frequencies of vibration. The three degrees left out are the three translations of the 16-atom group. They are represented in Table I as a continuous spectrum of frequencies stretching down to zero. We shall now proceed to justify and explain this entry in greater detail.

The translations of an atomic group within a crystal would necessarily tend to displace neighbouring atomic groups and hence would set up forces resisting the movement. We are therefore led to conclude that the degrees of freedom which do not appear as internal vibrations of our dynamic units would manifest themselves as internal vibrations in elementary volumes of larger dimensions. The larger such an element of volume is, the lower would be the limit of its possible frequencies of vibration. Hence, the translations of our atomic groups would be associated with vibrational movements in the crystal whose frequencies extend from the upper limit set by the frequencies of their internal vibration down to very low values. In other words, the vibration spectrum of diamond with its discrete set of frequencies would be supplemented by a residual spectrum which is continuous and extends down to zero frequency.

We have now to determine how the modes of vibration referred to above are distributed with respect to frequency in the residual spectrum. Low frequencies arise from internal vibrations in volume elements of large size. The number of such elements included within the crystal diminishes rapidly with increase of their linear dimensions. It follows that the density of the vibrational modes in the residual spectrum would fall off quickly as their frequency diminishes.

#### 4. THE CHARACTERS OF THE RESIDUAL SPECTRUM

The considerations set forth above may be put into a quantitative form. Consider an element of volume whose linear dimensions are  $m$  times as great as that of our 16-atom group. The number of such groups included in the crystal being denoted by  $N$ , the number of elementary volumes whose linear dimensions are  $m$  times greater would be  $N/m^3$ . The larger  $m$  is, the lower would be the frequencies of internal vibration in the element under consideration. We denote by  $\nu_m$ , the lowest of these frequencies. If  $m$  be replaced by  $n$ , the corresponding number of volume elements would be  $N/n^3$  and the lower limit of frequency would be denoted by  $\nu_n$ . Thus the part of the vibration spectrum included between  $\nu_m$  and  $\nu_n$  may be ascribed to  $3N(1/m^3 - 1/n^3)$  oscillators. It is evident that  $\nu_m$  and  $\nu_n$  would depend on the linear dimensions of the oscillators, and if we assume that  $\nu_m = f/m$ , and  $\nu_n = f/n$ , where  $f$



is a quantity having the dimensions of a frequency, we find that the spectral region between  $\nu_m$  and  $\nu_n$  would be associated with  $3N (\nu_m^3 - \nu_n^3)/f^3$  oscillators. In the limit as  $m$  approaches  $n$ , we may write  $\nu_m - \nu_n = d\nu$  and  $(\nu_m^3 - \nu_n^3) = 3\nu^2 d\nu$ . Thus, the  $3N$  available degrees of freedom would be distributed over the spectrum as indicated by the quantity  $3N \cdot 3\nu^2 d\nu/f^3$ . Integrating this over the entire range of the continuous spectrum, we should regain  $3N$ . Thus, we find  $f$  to be the upper limit of the continuous spectrum, its lower limit being zero.

The law of distribution of frequencies in the residual spectrum thus determined rests on the assumption that the frequencies of vibration of the volume elements considered are inversely proportional to their linear dimensions. This assumption is certainly valid when the oscillators are of sufficiently large dimensions. But it should be remarked that the distribution formula deduced on the basis of the assumption shows quite clearly that the great majority of the oscillators which contribute sensibly to the thermal energy are not much larger in size than our 16-atom groups. A further remark which should also be made is that we do not distinguish between the different possible modes of vibration of the volume elements, as for example, whether the vibrations are of the compressional or of the distortional type.

We have next to determine the value which should be assumed to be the upper limit of frequency in the residual spectrum. Since the spectrum owes its origin to the translatory movements of our 16-atom groups, the highest frequency appearing in it cannot exceed the lowest of the discrete frequencies of internal vibration of those groups which is  $624 \text{ cm.}^{-1}$ . We may, therefore, provisionally assume  $624 \text{ cm.}^{-1}$  to be also the upper limit at which the frequency distribution derived on the basis of our assumptions abruptly terminates. It is clear that the entire procedure is a simplification adopted to enable us to evaluate the atomic heat of diamond over the entire range of temperature in terms of well-known functions of which the tabulated values are available. We shall later consider the amendments needed to bring it into closer accord with the facts.

## 5. THE EXPERIMENTAL DATA

The graph depicting the variation of the atomic heat of diamond with temperature consists of three parts. The first part appears in the low temperature range between  $0^\circ$  and  $100^\circ \text{ K.}$  In this range, the atomic heat is very small, being only a few units in the second decimal place. In the second range which lies between  $100^\circ$  and  $300^\circ \text{ K.}$  the atomic heat rises steeply,



reaching a value of about 1.5 at room temperature. The third part of the range extends from 300° K. to the highest temperatures for which the experimental data are available. It is to be noted that even at 1000° K, the atomic heat is only about 5, in other words distinctly smaller than the theoretical limit of 5.94.

The measurements of H. F. Weber already referred to (*Philosophical Magazine*, 1875, 49, 161) showed clearly that the atomic heat of diamond falls off rapidly as the temperature is lowered, and that *per contra*, it increases as the temperature is raised but not so quickly, the graph of the variation showing a point of inflexion at about 400° K. More complete and accurate data than those of Weber in the temperature range from 275° K. to 1000° K. are available from the determinations by Magnus and Hodler (*Annalen Der Physik*, 1926, 80, 808). In the lower ranges of temperature, measurements have been made by K. S. Pitzer (*Journal of Chemical Physics*, 1938, 6, 68), by De Sorbo (*Ibid.*, 1953, 21, 876), and most recently by Desnoyers and Morrison (*Philosophical Magazine*, 1958, 3, 42). In the temperature range between 100° K. and 300° K. the measurements by these authors are in fair agreement with each other. But in the low temperature range between 0° K. and 100° K. where the atomic heat is very low and the measurements are therefore more difficult, there are considerable discrepancies between them. In the comparison between theory and experiment which will be made in the present memoir, we shall make use exclusively of the data of Desnoyers and Morrison, as these cover the entire range between 0° K. and 278° K. at short intervals. For the higher temperatures, the data reported by Magnus and Hodler are utilized. The experimental data of these authors are presented in a summarised form in Tables II and III below.

TABLE II

*Interpolated experimental values of atomic heats  
by Desnoyers and Morrison*

Temperature	20° K.	30° K.	40° K.	50° K.	60° K.	70° K.	80° K.	90° K.	100° K.
Atomic heat	0.00034	0.00117	0.00285	0.00564	0.01004	0.01676	0.02635	0.04030	0.05832

Temperature	120° K.	140° K.	160° K.	180° K.	200° K.	220° K.	240° K.	260° K.
Atomic heat	0.1115	0.1893	0.2915	0.4172	0.5624	0.7271	0.9050	1.0957



TABLE III

*Experimental values of atomic heats by Magnus and Hodler*

Temperature	300° K.	400° K.	500° K.	600° K.	700° K.	800° K.	900° K.	1000° K.
Atomic heat	1.522	2.417	3.162	3.771	4.255	4.625	4.890	5.059

It is obvious that the data covering such a great range of temperature and presenting such enormous variations in the quantity measured offer a most stringent test for the theory. As has been already remarked, the evaluation of the atomic heats is based entirely on the spectroscopically determined vibration frequencies, and no use is made of any other data or arbitrary constants. It is not possible to present the comparison between the results of the theoretical computation and the experimental data with the aid of only a single graph. In the lowest part of the temperature range, such a graph would be nearly coincident with the axis along which the temperature is plotted. Even in the second part of the temperature range, the ordinates would have to be presented on a large scale for a satisfactory comparison to be possible. Accordingly, the comparison is here made in three separate figures. Figure 1 below exhibits the over-all agreement between theory and experiment, the data for the entire range of temperatures being represented on a suitable scale. In Fig. 2, the data for the temperature range between 0° K. and 160 K. are presented, a much larger scale being adopted for the ordinates. In Fig. 3, the temperature range between 160° K. and 300° K. is similarly covered, but with the ordinates drawn on a less highly enlarged scale.

## 6. COMPUTATION OF THE ATOMIC HEATS

The procedure adopted for the evaluation of the atomic heat will be evident from Tables IV, V and VI where the calculations are shown in detail. The Einstein functions which give the atomic heat in terms of the characteristic frequencies and the absolute temperature are multiplied by their respective degeneracies and divided by 48. These are entered in the tables. The contribution of the residual spectrum to the atomic heat at the respective temperatures is entered below those of the discrete frequencies. This contribution is obtained by an integration of the Einstein function multiplied by the weight-factor given by the distribution law over the whole range of frequencies appearing in the residual spectrum. The final result is divided by 48 as in the case of the discrete frequencies. It is then added to the contribution



TABLE IV

*Computation of the atomic heats*

	20° K.	30° K.	40° K.	50° K.	60° K.	70° K.	80° K.	90° K.	100° K.
3 E <sub>1</sub> (1332)	..	..	..	..	..	..	..	..	..
8 E <sub>2</sub> (1273)	..	..	..	..	..	..	..	..	..
6 E <sub>3</sub> (1219)	..	..	..	..	..	..	..	..	..
4 E <sub>4</sub> (1176)	..	..	..	..	..	..	..	..	..
3 E <sub>5</sub> (1087)	..	..	..	..	..	..	..	..	..
3 $\Sigma_6$ (1087)	..	..	..	..	..	..	..	..	..
4 E <sub>7</sub> (1010)	..	..	..	..	..	..	..	..	..
6 E <sub>8</sub> (746)	..	..	..	..	..	..	0.0002	0.0006	0.0016
8 E <sub>9</sub> (624)	..	..	..	..	..	0.0004	0.0014	0.0041	0.0092
3 D (624)	0.0003	0.0011	0.0025	0.0048	0.0084	0.0132	0.0195	0.0273	0.0367
Atomic heat	0.0003	0.0011	0.0025	0.0048	0.0084	0.0136	0.0211	0.0320	0.0475

TABLE V

*Computation of the atomic heats*

	120° K.	140° K.	160° K.	180° K.	200° K.	220° K.	240° K.	260° K.	280° K.
3E <sub>1</sub> (1332)	..	0.0001	0.0003	0.0009	0.0021	0.0043	0.0074	0.0118	0.0174
8E <sub>2</sub> (1273)	..	0.0003	0.0012	0.0035	0.0079	0.0153	0.0259	0.0402	0.0578
6E <sub>3</sub> (1219)	0.0001	0.0004	0.0014	0.0036	0.0082	0.0151	0.0248	0.0373	0.0527
4E <sub>4</sub> (1176)	0.0001	0.0004	0.0013	0.0033	0.0069	0.0121	0.0200	0.0295	0.0408
3E <sub>5</sub> (1087)	0.0001	0.0006	0.0018	0.0043	0.0084	0.0143	0.0220	0.0312	0.0419
3E <sub>6</sub> (1087)	0.0001	0.0006	0.0018	0.0043	0.0084	0.0143	0.0220	0.0312	0.0419
4E <sub>7</sub> (1010)	0.0003	0.0015	0.0042	0.0092	0.0170	0.0275	0.0405	0.0554	0.0721
6E <sub>8</sub> (746)	0.0071	0.0190	0.0384	0.0646	0.0966	0.1311	0.1684	0.2042	0.2402
8E <sub>9</sub> (624)	0.0289	0.0632	0.1094	0.1634	0.2219	0.2799	0.3374	0.3905	0.4401
3D (624)	0.0587	0.0838	0.1096	0.1347	0.1584	0.1796	0.1992	0.2162	0.2313
Atomic heat	0.0954	0.1699	0.2694	0.3918	0.5358	0.6935	0.8676	1.0475	1.2362



TABLE VI

Computation of the atomic heats

		300° K.	400° K.	500° K.	600° K.	700° K.	800° K.	900° K.	1000° K.
3E <sub>1</sub> (1332)	..	0.0240	0.0692	0.1201	0.1658	0.2029	0.2327	0.2560	0.2747
8E <sub>2</sub> (1273)	.	0.0782	0.2104	0.3516	0.4713	0.5703	0.6460	0.7054	0.7501
6E <sub>3</sub> (1219)	..	0.0700	0.1764	0.2844	0.3760	0.4465	0.5017	0.5426	0.5757
4E <sub>4</sub> (1176)	..	0.0536	0.1371	0.2020	0.2617	0.3080	0.3436	0.3696	0.3902
3E <sub>5</sub> (1087)	..	0.0530	0.1157	0.1712	0.2147	0.2466	0.2713	0.2895	0.3029
3E <sub>6</sub> (1087)	..	0.0530	0.1157	0.1712	0.2147	0.2466	0.2713	0.2895	0.3029
4E <sub>7</sub> (1010)	..	0.0896	0.1785	0.2518	0.3069	0.3482	0.3773	0.3986	0.4159
6E <sub>7</sub> (746)	..	0.2746	0.4159	0.5086	0.5709	0.6119	0.6398	0.6589	0.6764
8E <sub>9</sub> (624)	..	0.4862	0.6552	0.7589	0.8219	0.8643	0.8924	0.9128	0.9269
3D (624)	..	0.2449	0.2911	0.3173	0.3326	0.3426	0.3491	0.3540	0.3573
Atomic heat	..	1.4271	2.3652	3.1371	3.7365	4.1879	4.5252	4.7769	4.9730

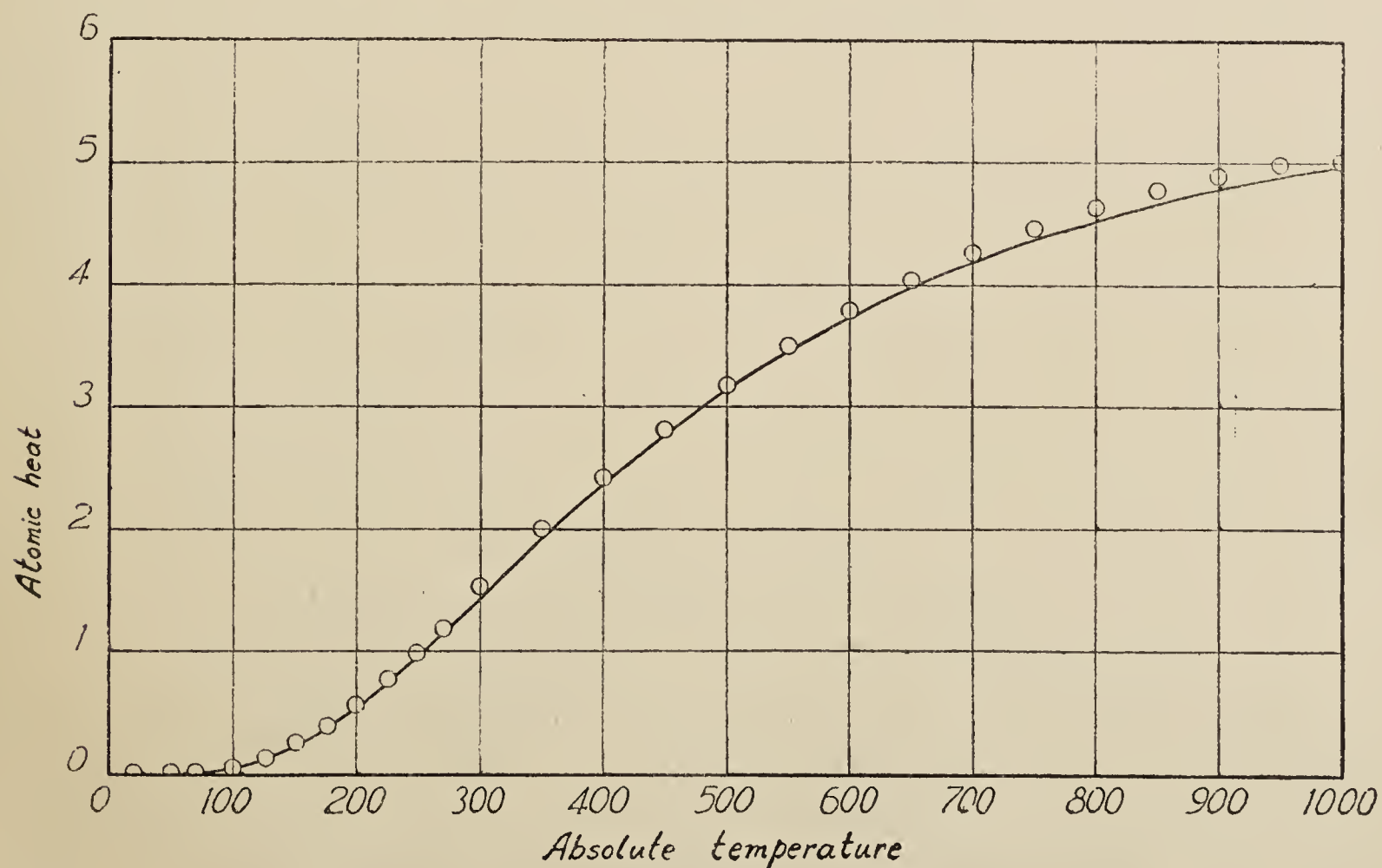


FIG. 1. Comparison of Calculated and Observed Atomic Heats.

Calculated atomic heats ———, Experimental data ○○○○



of the discrete frequencies of vibration to the atomic heat at each of the temperatures listed in the table.

It will be seen from Tables IV, V and VI that in the lowest part of the temperature range between  $0^{\circ}$  K. and  $100^{\circ}$  K. the atomic heat is determined entirely or principally by the contribution of the residual spectrum of frequencies, the discrete frequencies being altogether too high to be thermally excited. In the second part of the temperature range between  $100^{\circ}$  K. and  $300^{\circ}$  K. the energy of vibration associated with the discrete frequencies rapidly mounts up with rising temperature, while on the other hand, the contribution of the residual spectrum increases less rapidly; it progressively approaches its limiting value which is  $1/16$ th of the theoretical limit for the total atomic heat.

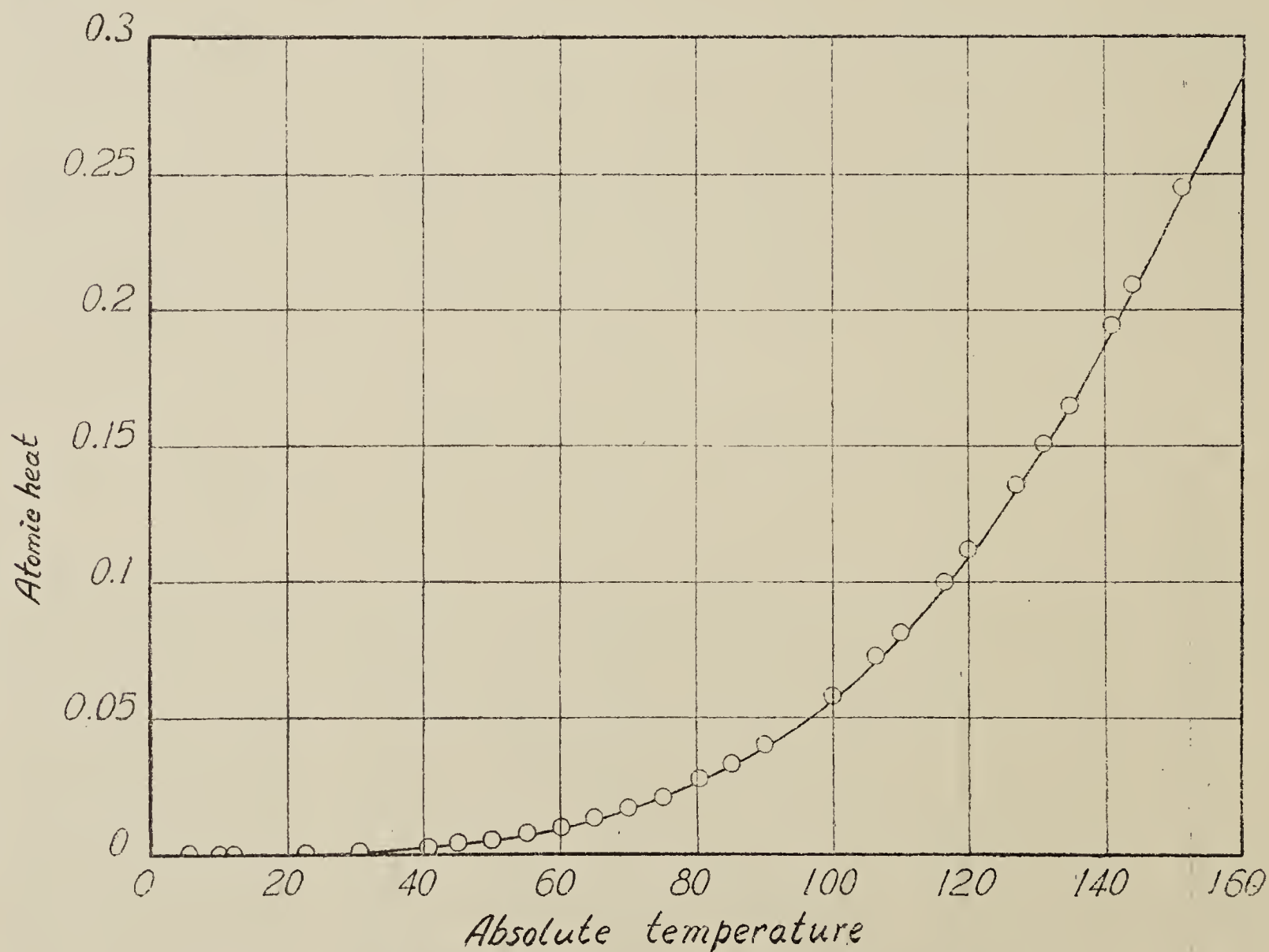


FIG. 2. Comparison of Calculated and Observed Atomic Heats.  
Calculated atomic heats ———. Experimental data ○○○○

We may here make some remarks on the comparison between the results of theory and experiment exhibited in Fig. 1. While there is an excellent over-all agreement, divergences of a few per cent. appear at temperatures above  $600^{\circ}$ . The origin of these discrepancies is not far to seek. The characteristic frequencies used are those determined with the diamond held



at room temperature. The changes in these frequencies which manifest themselves as the temperature is raised are small but are by no means negligible. For example, the highest frequency which is  $1332\text{ cm.}^{-1}$  at ordinary temperatures goes down to  $1318\text{ cm.}^{-1}$  at  $1000^\circ$ . The change is evidently associated with the thermal expansion of the crystal and it is to be expected that all the characteristic frequencies would likewise be diminished by small percentages. The atomic heats if calculated on the basis of the diminished frequencies would necessarily be greater. In view, however, of the uncertain accuracy of the experimental data at the higher temperatures, this matter will not be further pursued here.

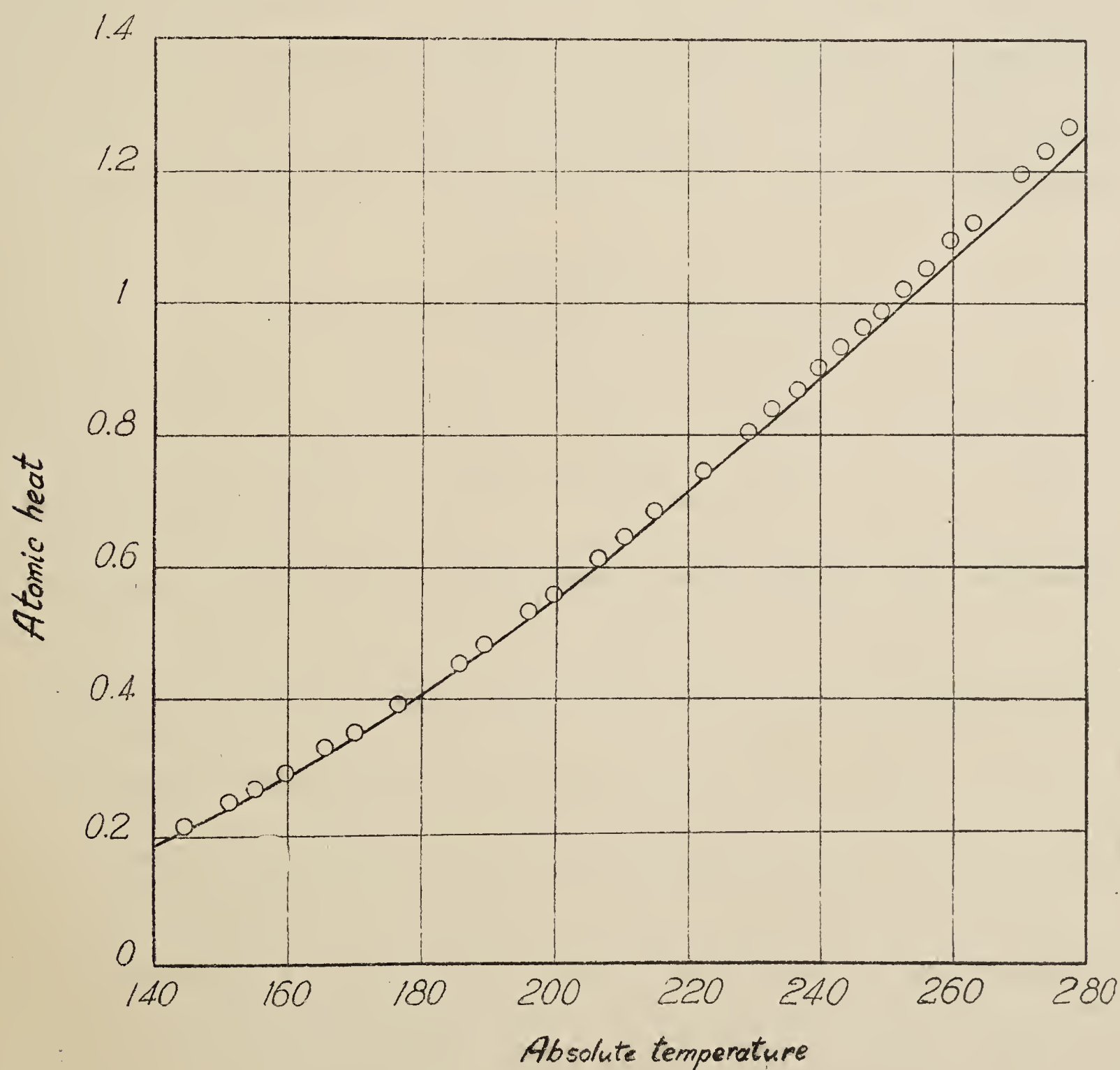


FIG. 3. Comparison of Calculated and Observed Atomic Heats.  
Calculated atomic heats ———, Experimental data ○○○○



## 7. THE LOW TEMPERATURE SPECIFIC HEATS

A comparison of the figures in Tables II and IV shows that at the very lowest temperatures, the computed and observed atomic heats are in good agreement with each other. Disagreements however appear at higher temperatures, the calculated values being distinctly smaller than the observed ones. The percentage differences are greatest at about  $100^{\circ}$  T and become smaller at higher temperatures. It is evident that these discrepancies arise from the assumption made in our calculations that the upper limit of frequency in the residual spectrum is the same as the lowest of the discrete frequencies of vibration, viz.,  $624 \text{ cm.}^{-1}$ . That a somewhat smaller value for the limit should be assumed as the basis of the calculation is indicated by various considerations, including especially the evidence furnished by studies on the blue luminescence spectra of diamond held at liquid-air temperatures. The vibration spectrum of diamond manifests itself in these spectra in combination with the electronic transition giving rise to the luminescence and it is

TABLE VII

*Re-computation of theoretical atomic heats*

Temperature	$20^{\circ}$ K.	$30^{\circ}$ K.	$40^{\circ}$ K.	$50^{\circ}$ K.	$60^{\circ}$ K.	$70^{\circ}$ K.	$80^{\circ}$ K.	$90^{\circ}$ K.	$100^{\circ}$ K.
3 D (575)	0.0004	0.0014	0.0032	0.0062	0.0106	0.0168	0.0247	0.0343	0.0456
Atomic heat	0.0004	0.0014	0.0032	0.0062	0.0106	0.0172	0.0263	0.0390	0.0564

Temperature	$120^{\circ}$ K.	$140^{\circ}$ K.	$160^{\circ}$ K.	$180^{\circ}$ K.	$200^{\circ}$ K.	$220^{\circ}$ K.	$240^{\circ}$ K.	$260^{\circ}$ K.	$280^{\circ}$ K.
3 D (575)	0.0713	0.0992	0.1270	0.1530	0.1769	0.1981	0.2162	0.2326	0.2467
Atomic heat	0.1081	0.1853	0.2868	0.4101	0.5543	0.7123	0.8846	1.0639	1.2516

Temperature	$300^{\circ}$ K.	$400^{\circ}$ K.	$500^{\circ}$ K.	$600^{\circ}$ K.	$700^{\circ}$ K.	$800^{\circ}$ K.	$900^{\circ}$ K.	$1000^{\circ}$ K.
3 D (575)	0.2592	0.3017	0.3246	0.3383	0.3468	0.3525	0.3566	0.3594
Atomic heat	1.4414	2.3758	3.1444	3.7422	4.1921	4.5286	4.7795	4.9751



noticed that there is a large and sudden drop in its intensity at a point distant about  $575\text{ cm.}^{-1}$  from the electronic transition. There is some justification therefore for taking  $575\text{ cm.}^{-1}$  instead of  $624\text{ cm.}^{-1}$  as the upper limit of frequency in the residual spectrum.

In Figs. 2 and 3, a comparison is made of the experimental data with the theoretically computed atomic heats in the lower ranges of temperature, viz., from  $0^\circ$  to  $160^\circ\text{ A}$  and from  $140^\circ$  to  $180^\circ\text{ A}$ , the observational values being those of Desnoyers and Morrison, and the theoretical values being those recalculated taking  $575\text{ cm.}^{-1}$  to be the upper limit of frequency in the residual spectrum, as shown in Table VII. The agreement now obtained between the calculated and observed atomic heats is satisfactory. It is especially good in Fig. 2.







## THE DIFFRACTION OF X-RAYS BY DIAMOND: PART I

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(Memoir No. 109 of the Raman Research Institute, Bangalore-6)

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### 1. INTRODUCTION

BY reason of its remarkable physical properties, diamond stands out uniquely as the crystal which shows us the way to a correct understanding of the fundamental aspects of the physics of the solid state. The atomic vibrations in crystals, the theory of their specific heats and their spectroscopic behaviour may be mentioned in this connection. These topics formed the subject of recent memoirs published in these *Proceedings*, and the experimental results obtained with diamond figured very prominently in them. The present communication deals with the X-ray diffraction effects exhibited by diamond and considers them both from the theoretical and experimental standpoints. It emerges that diamond has a great deal to teach us regarding the fundamental aspects of the subject of X-ray crystallography and indeed compels us to approach the subject from new points of view.

The present investigation stems from a report from the author's laboratory published in the year 1940 under the title "A New X-Ray Effect" (*Current Science*, 1940, 9, 165-67). That report recorded the discovery of the very striking and indeed surprising features which reveal themselves in strongly exposed X-ray diffraction patterns of diamond. It was very clear that the phenomena stood outside the framework of the classical theory of X-ray diffraction. It was accordingly suggested that they had their origin in the quantum-mechanical excitation of the atomic vibrations in diamond by the monochromatic X-ray beam traversing it, the X-rays being themselves reflected as a result of such excitation with a change of frequency. It was explained in the report why it was possible for reflections of this nature to be observed even when the setting of the crystal was different from that ordinarily required for a reflection of the X-rays by the same lattice planes.

The instrumental equipment available for the research at that time was, unfortunately, not of sufficient power to enable the subject to be explored with any degree of completeness. The investigation had accordingly to be laid aside and the circumstances in which the author found himself did not,



for many years, permit of its being resumed. Happily, however, it has now been possible to take up the work once again, not only with new and more powerful instrumental aid, but also with fresh theoretical ideas derived from the work of the author in the related fields referred to earlier in this introduction. The results are now laid before the reader.

Part I of the paper considers the theory of X-ray diffraction by crystals in general from a fundamentally new standpoint. Part II considers the application of the theory to the particular case of diamond. Part III presents the results of a detailed experimental investigation of the case.

## 2. THE STRUCTURE OF CRYSTALS

The conventional view of a crystal as an assembly of atoms arranged in a regular three-dimensional array in space is neither useful nor enlightening when we seek to obtain an insight into the behaviour of crystals when traversed by radiation in the different ranges of frequency. It is necessary indeed to lay aside that view and regard a crystal as a system composed of two kinds of charged particles, namely the nuclei and the electrons, their relative numbers being determined by the magnitudes of their charges. Diamond, for example, is an assembly of carbon nuclei and of electrons, the latter being six times as numerous as the former.

The atomic nuclei have enormously larger masses than the electrons and it is this circumstance that determines the manner in which the two sets of particles arrange themselves in space. According to the fundamental notions of the quantum theory, it is not meaningful to regard the electrons as located at any specifiable points in space, while on the other hand, it is permissible to do so in respect of the nuclei. The Coulomb forces exerted by the nuclei on the electrons tend to draw the latter together and hold them in dynamic equilibrium. Accordingly, what may be described as a cloud of negative charge gathers round each nucleus. But when we raise the question as to what determines the position of the nuclei in space, the answer, remarkably enough, is to be found in these very clouds of negative charge which each nucleus gathers around itself. Indeed, it is the electrons which determine the location and ordering in space of the nuclei. Accordingly, it would be appropriate to describe a crystal as consisting of two distinct assemblies, namely an assembly of nuclei whose positions it is possible to specify with some measure of precision, and an assembly of electrons. It is the interaction of these two assemblies with each other that determines the architecture of the crystal and its physical behaviour. This view of crystal structure will be found most illuminating when we proceed to consider the phenomena resulting from the passage of radiation through the crystal.



### 3. THE RESPONSE OF CRYSTALS TO RADIATION

The tremendous disparity in the masses of the nuclei and of the electrons justifies us in ignoring any movement of the atomic nuclei which results directly from the action of the electric field of the radiation on the charges carried by the nuclei. What we need consider in every case is the effect of the radiation field on the electronic clouds. But since these are held in place by their interactions with the atomic nuclei, the latter would also tend to be disturbed when the electronic clouds are set in motion by the field. These considerations are valid irrespective of the individual features of the crystal structure and of the frequency or wavelength of the incident radiation. But since the response of the electrons to the field of the incident radiation would depend on these latter factors, the nature and extent of the movements of the atomic nuclei consequent thereon would also be influenced by those factors.

We may illustrate the foregoing remarks by considering first the cases in which the frequency of radiation lies in the infra-red range. Viewing the matter classically, the effect of the radiation on the electronic clouds in this case would be to produce periodic displacements to and fro of the electronic clouds with the same frequency. These displacements would, however, be limited by the binding of the electrons to the nuclei. Even when the frequency of the incident radiation coincides with a natural frequency of vibration of the atomic nuclei about their positions of equilibrium, it would not necessarily follow that such vibration is excited by the field. Indeed, it is well known that in many cases, the field does not excite the vibrations, in other words, the vibrations are not active in the absorption of the infra-red radiation. In order that any given mode of vibration should be excited by the incident radiation field and thereby rendered infra-red active, it is necessary that a certain lack of symmetry in the structure of the crystal or of the particular mode of vibration results in the movements of the nuclei being accompanied by a periodic displacement to and fro of the electronic clouds which hold the nuclei together. The selection rules which define the conditions under which any particular mode of vibration is active in the absorption of infra-red radiation are, indeed, based on considerations of this nature. That they are in agreement with experience demonstrates the validity of the present approach to the subject.

Coming now to the case of visible light, the response of the crystal to the field of the incident radiation would be determined by the relation between the frequencies of the incident radiation and the characteristic frequencies of vibration of the electronic clouds. Further, since the frequency of the radiation



is much higher than the natural frequencies of vibration of the nuclei' the possibility of the incident radiation exciting the latter in the manner considered in the preceding paragraph would not arise at all. There are however possibilities of the nuclear vibrations being excited by the electronic movements in a different way. Considering those electrons which hold together the different nuclei and thus form part of the architecture of the crystal, it is evident that any approach or recession of such nuclei from each other would influence the characteristic frequencies of the electronic clouds attached to them. This is equivalent to stating that the response of the electronic clouds to the field of the incident light would be modified or modulated by the natural frequencies of the nuclear vibrations. That such an effect actually arises is demonstrated by the fact that when monochromatic light traverses a crystal, and the light diffused in its interior is spectroscopically examined, monochromatic radiations are observed in it whose frequencies differ from that of incident light by amounts equal to the characteristic infra-red vibration frequencies. Whether or not any particular mode of vibration of the nuclei thus reveals itself is determined by the circumstances of the case. The selection rules which express these circumstances are naturally different from those that determine the activity in infra-red absorption.

The frequency of X-radiation is very much higher than that of either visible light or of infra-red waves, and the phenomena arising from their passage through crystals would naturally be determined by the high frequencies and correspondingly short wavelengths of the rays. We have, in the first instance, to consider the effect of the radiation field on the electronic clouds. But it is not possible to ignore the fact that the electronic clouds are held in their places by the atomic nuclei and that, consequently, not only the electronic clouds but also the atomic nuclei would tend to be disturbed by the X-radiation. There is every reason therefore to expect that the effects arising from such disturbance of the nuclei would manifest themselves in the X-ray diffraction patterns of the crystal.

The foregoing represents the general point of view which will be developed and discussed in greater detail in the present series of papers. Its consequences will also be compared with the facts of observation. We shall find that it receives the clearest possible support in the phenomena exhibited by diamond in its X-ray diffraction patterns.

#### 4. X-RAYS AND CRYSTALS

The observational basis of X-ray crystallography is the selective reflection of X-rays by the atomic layers in a crystal at angles of incidence determined by the wavelength of X-rays and the spacing of the layers. The phe



nomenon is clearly analogous to the familiar effect of iridescence exhibited by regularly stratified media on which visible light is incident. Hence it is quite natural to explain the phenomena of X-ray diffraction by crystals on similar lines. We assume the crystal to be a material of which the optical polarisability for X-ray frequencies exhibits space-periodic variations in three dimensions. A determination of the settings of the crystal at which the X-ray reflections for a known wavelength are observed enables us to determine the spacings of the stratifications in various directions as also their relative orientations. A comparative study of the intensities of the various reflections enables us to go further and obtain a measure of the magnitude of the periodic variations of the polarisability for X-ray frequencies appearing in each set of stratifications. The entire procedure is phenomenological in character. In endeavouring to deduce from the experimental results a picture of the ultimate structure of the crystal, various difficulties arise which we shall not discuss here. What we are actually concerned with is the meaning of the phrase “Polarisability for X-Ray Frequencies” employed above in terms of the ultimate structure of the crystal.

In classical optics, where we are concerned with the behaviour of media which can be regarded as continuous, the term polarisability has a simple and definable meaning, namely, the strength of the electric dipole per unit of volume induced by an external electric field of unit strength. Difficulties arise when we endeavour to take over this description into the region of high frequencies and short wavelengths. These difficulties are of two kinds. Firstly, the medium can no longer be regarded as a continuous and structureless substance, since it actually consists of a set of discrete particles arranged in layers. The second difficulty is that these particles are not all similar and similarly circumstanced. In particular, the nuclei and the electrons have very different masses and are oppositely charged; the interactions between them enter fundamentally into the problem of determining the response of the medium to the field of the incident radiation.

A way of escape from the difficulties indicated above may be sought for by regarding the recognisable units in the structure as “diffracting particles” in the sense of classical optics. We find however that such a procedure is not sustainable. For example, the individual electrons in the crystal cannot be assigned the role of “diffracting units”. For, as already remarked, an electron does not possess any precisely definable location in space and hence the phase of any radiation that it could diffract would be indeterminate. An even more fundamental difficulty is that if an individual electron does interact with X-rays, the result is a secondary radiation of



altered wavelength, in other words the Compton type of scattering. The alternative approach of regarding the individual *atoms* in the crystal as the 'diffracting units' is also not sustainable. For, in any actual crystal, the atoms are held in their places by the electrons which link them together and these electrons cannot therefore be regarded as the exclusive possession of any particular atom. Taking for instance the case of diamond, only two out of every six electrons can with any measure of justification be considered as attached to an individual carbon nucleus. The remaining four electrons enter into the architecture of the crystal and hence must be considered as held in common with other atoms.

In view of the situation stated above, it is clear that the only logically sustainable approach to the subject of X-ray diffraction is that which proceeds on the following basis: *the X-ray reflections by a crystal are a co-operative effort of the entire structure, meaning thereby all the nuclei and all the electrons included in it.*

## 5. THE ENERGY LEVELS OF CRYSTALS

The present approach to X-ray diffraction problems differs from that customarily adopted in two respects. In the first place we recognize that the atomic nuclei have a part to play in the phenomena since on the one hand, they hold the electrons in place and on the other hand are themselves held in place by the electrons. Further, what we shall actually concern ourselves with is not the behaviour of the individual electrons or of the individual atoms in the crystal, but the behaviour of the two assemblies consisting of nuclei and of electrons respectively constituting the crystal when it is traversed by the X-radiation. This approach brings the phenomena of X-ray diffraction into the closest relationship with the behaviour of crystals when traversed by ultra-violet, visible or infra-red radiation. In all such cases we are concerned with the changes in the energy levels of a crystal which are or could be induced by the radiations traversing it. As we have two sets of particles which differ greatly in their masses, the possible changes in the energy levels are of two kinds which in the usual language of spectroscopy may be described as changes in the electronic levels and the vibrational levels respectively. The simplest cases are those in which there is no change in either the electronic or vibrational energy states of the crystal when traversed by radiation. This would correspond to a simple undisturbed transmission of the radiation through the crystal in the case of visible or ultra-violet light. In the case of X-radiation, however, the stratifications of optical polarisability in the structure of the crystal can in appropriate circumstances result in geometric reflections of X-rays in various directions. In the language of the



quantum theory, such reflections would be described as the result of an exchange of momentum without an exchange of energy between the radiation and the crystal. Still another possibility has to be recognised, namely, that while the initial and final *electronic* energy states are the same, the radiation induces a change in the *vibrational* energy level which persists. When and in what circumstances such a process can occur as the result of the passage of X-radiation, and what would be the observable results of such a process are the questions which we shall proceed to consider.

The answers to the questions raised above emerge when we consider the effects observed respectively when a crystal is traversed by radiation in the infra-red and in the visible regions of the spectrum. In the former case we are concerned with an actual absorption of the radiation. In the latter case we have a simple transmission accompanied by a diffusion or scattering with shifts of frequency indicating that changes in the vibrational energy levels have been induced by the incident light. It should not be imagined that each and every characteristic mode of vibration can manifest itself in the infra-red absorption spectrum and in the scattering of light as a frequency shift. This is very far indeed from being the case. Whether a particular mode of vibration does or does not so manifest itself is determined by certain selection rules which are different for infra-red absorption and for light-scattering. Why this is so becomes clear when the mechanisms respectively of infra-red absorption and of the scattering of light with change of frequency are examined. The latter effect is explained as arising from the variations of the optical polarisability of the crystal for visible light which accompany changes in its infra-red energy levels. On the other hand, infra-red absorption arises from the displacements of electric charge produced by the incident radiation. The question arises whether effects of the same nature can be induced by X-radiation. It is obvious that any change in the optical polarisability for X-rays produced by the changes in the infra-red energy levels of the crystal would, in view of the very high frequencies of X-radiation, be entirely negligible. On the other hand, the periodic displacements of electric charge associated with vibrational transitions which are active as absorbers of infra-red radiation necessarily involve periodic displacements of the stratifications of optical polarisability which give us the X-ray reflections by the crystal. *It follows that when X-radiations traverse a crystal, they can induce changes in its vibrational energy levels, provided such changes involve displacements of electric charge—in other words, provided that the modes of vibration under reference are active as absorbers of infra-red radiation.*



## 6. X-RAY REFLECTION WITH CHANGE OF FREQUENCY

We have now to consider what would be the consequences of a change in the vibrational energy levels of crystals induced by X-rays in the circumstances stated above. The question arises whether the observable result of such a process would be a diffusion of the X-rays in various directions or else a reflection similar to that ordinarily observed involving no exchange of energy. Before this can be answered, we have to ask ourselves: What is the nature of the vibration spectrum of a crystal? This question has already been dealt with by the author in various recent publications and the same ground need not therefore be traversed here once again. As has been shown in the publications referred to, theory and experiment alike indicate that the vibration spectrum of a crystal containing  $p$  atomic nuclei in each unit cell consists of a set of  $(24p - 3)$  monochromatic frequencies, accompanied by a residue representing the three omitted degrees of freedom which constitutes a continuous spectrum of low frequencies. Amongst the  $(24p - 3)$  modes, in  $(3p - 3)$  modes which are the only ones with which we are concerned in the present paper, the vibration repeats itself with identical frequency and amplitudes and phases in the successive cells of the crystal structure. It follows from this that the changes in the corresponding vibrational levels induced by the incident X-radiation would extend over the entire volume of the crystal traversed by the incident X-ray beam. As a consequence of this again, the X-rays would be regularly reflected by the stratifications of the crystal; such reflection involves a transfer of energy between the radiation and the crystal equal to the vibrational frequency multiplied by Planck's constant. *Hence, the frequency of the reflected X-rays would differ from that of the incident X-ray beam by the frequency of the vibrational mode excited.* As has been explained in the preceding section, such a process is only possible in respect of the modes of vibration which are active in the absorption of infra-red radiation.

The result stated above has a classical analogue in the reflection of light by a stratified medium which is assumed to execute oscillations of small amplitude normal to its layers. (An oscillation parallel to the layers would obviously be without effect.) It can readily be shown that, the reflected wave of the original frequency  $A \sin 2\pi\nu t$  would be accompanied by *two* additional components which are respectively of diminished and increased frequency, viz.,

$$\pi A d^* / d \sin 2\pi (\nu - \nu^*) t$$



and

$$\pi.A.d^*/d.\sin 2\pi (\nu + \nu^*) t$$

$d$  and  $d^*$  are respectively the spacing of the stratifications and the amplitude of their oscillation, while  $\nu$  and  $\nu^*$  are respectively the frequencies of the incident radiation and of the oscillation of the stratifications. The equality of amplitude of the reflected waves of enhanced and diminished frequency is a natural consequence of our assuming the oscillations of the layers to subsist of themselves. In the quantum theory, on the other hand, the oscillations are *induced* by the incident radiation, and hence the two components would, in general, be of very different intensities; their ratio is determined by thermodynamic considerations and is expressible in terms of the Boltzmann factor  $e^{-h\nu^*/kT}$ .

The classical analogy referred to above leads to some general inferences regarding the intensity of the X-ray reflections with altered frequency in relation to the intensity of the X-ray reflections of unmodified frequency given by the same set of lattice planes. We notice in the first place that the two are proportional to each other. Hence, if one is absent, the other would also be absent. In other words, the so-called missing reflections familiar to the X-ray crystallographer would also fail to manifest themselves as dynamic reflections. Further, we could normally expect to observe the latter only as accompaniments of the stronger reflections of the ordinary kind. Their relative intensity is determined by the square of the ratio  $d^*/d$ , where  $d^*$  is the amplitude of oscillation of the stratifications and  $d$  is their spacing. Since  $d^*$  is a measure of the displacement of electric charge which is responsible for the activity of the mode in the absorption of infra-red radiation, it follows, firstly, that inactive modes would not give rise to dynamic X-ray reflections, and secondly, that the greater the infra-red activity of a mode, the more intense would be the dynamic X-ray reflections associated with it.

## 7. THE PHASE-WAVES OF DYNAMIC REFLECTION

The possibility of X-radiation exciting one of the  $(3p - 3)$  characteristic modes of nuclear vibration and being itself reflected in the process was deduced above on the assumption that the wavelength of the X-rays, the spacing of the stratifications, and the angle of incidence on them are related to each other in the same manner as that necessary for a reflection of the ordinary kind. In these circumstances, the excited vibration necessarily repeats itself with the same frequency and also with the same amplitudes and phases in every cell of the structure traversed by the X-rays.

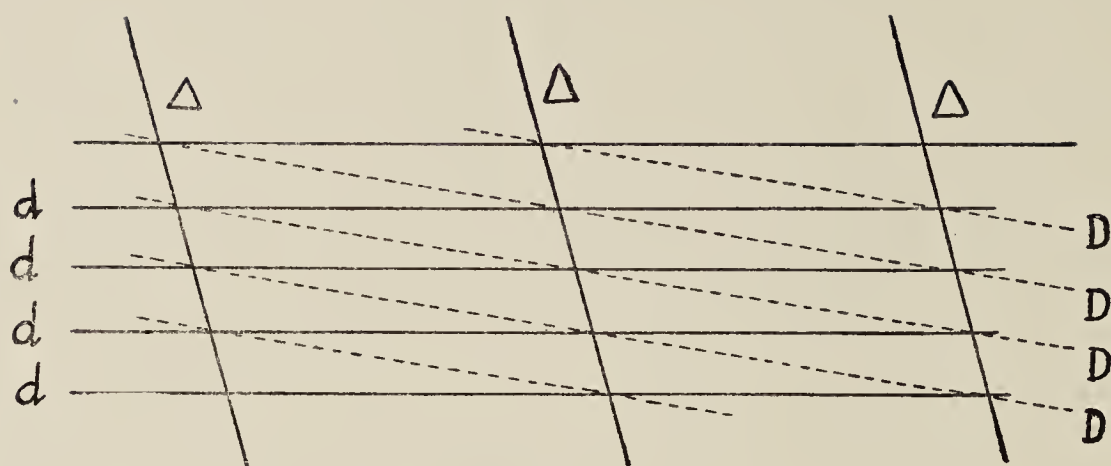


FIG. 1

For X-ray reflections with a change of frequency to be observable at other settings of the crystal, it is necessary that the vibrations excited are everywhere similar, but that the phase of the excited vibration in the individual cells of the structure alters progressively through the crystal in such a manner that the vibrations excited in all the irradiated cells conspire to give a coherent reflection. The condition for this to be possible is most readily stated in the form of a diagram (Fig. 1 in the text). The lines marked  $d d d$  represent the traces on the plane of the paper of the stratifications in the crystal. The planes marked  $\Delta \Delta \Delta$  similarly represent the traces on the plane of the paper of the *phase-waves*, in other words of the planes along which the internal vibrations of the crystal have identical phases. It is evident from the figure that the planes marked  $D D D$  cutting across both of them would represent the stratifications which play the same role for the dynamic reflections that  $d d d$  play for the static ones. The relationship between the spacings  $D$ ,  $d$  and  $\Delta$  is given by the vectorial formula

$$\frac{\vec{1}}{D} = \frac{\vec{1}}{d} + \frac{\vec{1}}{\Delta} \quad (1)$$

It needs to be explained why the situation indicated in Fig. 1 can arise consistently with the principles of dynamics and of the quantum theory. A vibration in which the frequency as well as the amplitudes and the phases are the same in every cell of the crystal structure is the only possible vibration having the characters of a normal mode. Since, however, the interatomic forces in crystals are essentially short-range forces, it is permissible to regard a crystal as made up of a great number of quasi-independent oscillators which have common modes and frequencies of vibration. Indeed, this is the approach which has necessarily to be adopted in developing the theory of the specific heats of crystals. It leaves out of account the small uncertainties in the frequency of vibration incidental to a limitation in size of the individual oscillators. In our present problem, therefore, it is permissible to consider



modes of internal vibration which are the same everywhere in the crystal but in which the phase of vibration in the individual cells alters progressively as we move through the crystal. If  $\Delta$  is large enough compared with  $d$ , the vibration would be practically indistinguishable from the limiting case in which  $\Delta$  is infinite. But as  $\Delta$  is diminished, what we have in the crystal is not a normal mode but a *forced* oscillation of which the frequency is different, the more so, the smaller  $\Delta$  is. In other words, a dynamic reflection in these circumstances results from a forced oscillation excited by the X-rays with a frequency differing slightly from that of the free oscillations of the structure. Hence, using the language of the quantum theory, we may infer that the probability of such an event happening would diminish rapidly as  $\Delta$  becomes smaller. In consequence, we would find that the dynamic reflection has the maximum intensity when the setting of the crystal is that at which the ordinary reflections also appear; the intensity would fall off rapidly as the crystal is moved away from that setting in either direction.

#### 8. THE GEOMETRIC LAW OF DYNAMIC REFLECTION

The construction shown in Fig. 1 enables us to deduce some general results regarding the geometric behaviour of the dynamic reflections. If the phase wavelength  $\Delta$  is infinite, the dynamic stratifications  $D D D$  would coincide with the static layers  $d d d$ . Hence, if the X-rays are incident on the latter at the correct angle for a regular reflection of the ordinary kind, the dynamic reflection would also appear in the same direction superposed on it. In the general case, the direction in which the reflection would appear would be determined by the orientation and the magnitude of the phase-vector. If both of these quantities can vary arbitrarily, then nothing in the nature of a regular reflection would be possible. If, however, the orientation of the phase-vector is precisely defined, a monochromatic X-ray beam incident at a precisely defined angle on the lattice planes of a crystal can result in a dynamic reflection also appearing in a precisely defined direction; but unlike the static reflection in similar circumstances, it would be observable over a wide range of settings of the crystal. The plane of reflection would naturally be the plane of incidence of the X-rays on the dynamic stratifications and the angles of incidence and of reflection with respect to them would also be equal.

Figure 2 exhibits the geometric laws of dynamic reflection of X-rays in a readily comprehensible fashion. The directions of the vectors  $1/\vec{d}$ ,  $1/\vec{D}$ ,  $1/\vec{\Delta}$  are represented by points on the surface of a sphere, the X-ray beam

being assumed to traverse the crystal along the polar axis of the sphere. Three meridional circles have been drawn on the sphere passing respectively through those three points. The first circle is evidently the plane of incidence

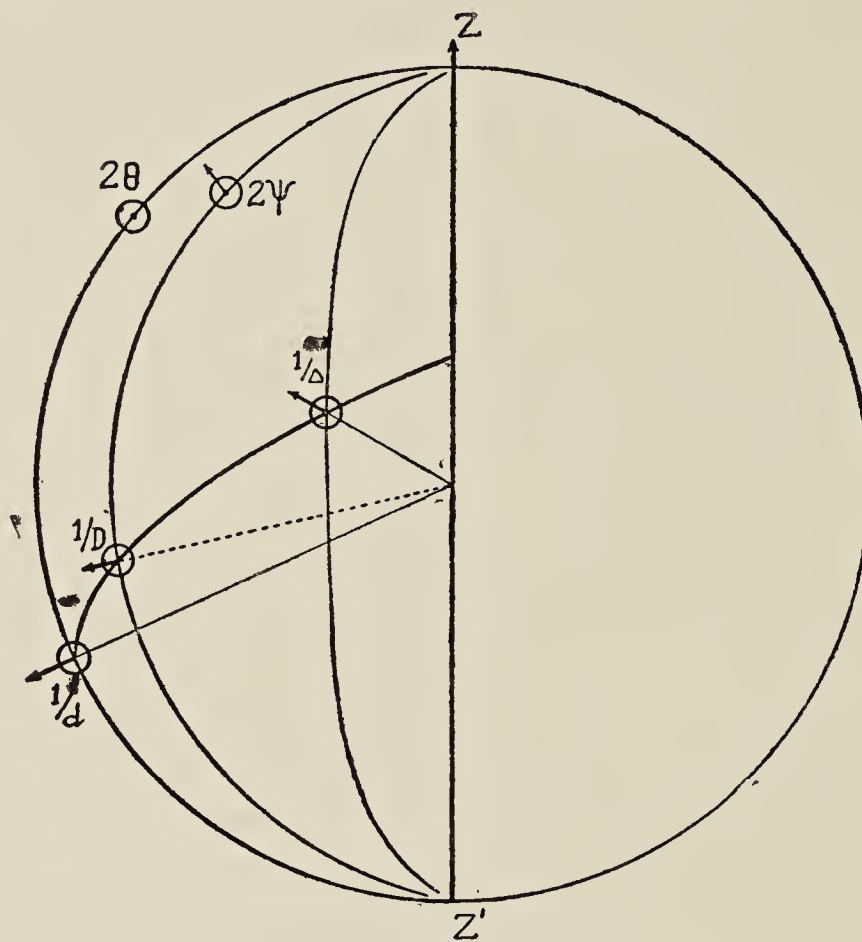


FIG. 2

of the X-rays on the lattice layers whose spacing is  $d$ . The second is the plane of incidence of the X-rays on the dynamic stratifications. The third circle is the plane containing the incident X-rays and the normal to the phase-waves. From equation (1) connecting the three vectors  $\vec{1/d}$ ,  $\vec{1/D}$  and  $\vec{1/\Delta}$ , it follows that the point representing  $\vec{1/D}$  on our sphere would lie on a great circle drawn through  $\vec{1/d}$  and  $\vec{1/\Delta}$ , its actual position on that circle being determined by the relative values of  $d$  and  $\Delta$ . If  $\theta$  be the glancing angle of incidence of the X-rays on the lattice layers of the crystal, a reflection would appear in a direction making an angle  $2\theta$  with the polar axis of the sphere on the first meridional circle, provided the condition  $2d \sin \theta = \lambda$  is satisfied. This would correspond to the case in which the phase wavelength  $\Delta$  is infinite. In the actual case to which the figure refers, the dynamic reflection would appear in a direction making an angle  $2\psi$  with the polar axis of the sphere,  $\psi$  being the glancing angle of the incident X-rays on the dynamic stratifications. It is here assumed that the condition  $2D \sin \psi = \lambda$  is satisfied. The figure indicates that the dynamic reflection deviates from the direction in which it would appear for an infinite phase wavelength, both along



the meridional circle and transverse to it, to extents determined by the angle between the first and the third meridional circles as also by the angle of incidence of the X-rays on the lattice planes under consideration.

## 9. SUMMARY

The theory of X-ray diffraction in crystals is discussed and it is shown that the X-ray reflections must be regarded as a co-operative effort of the entire structure in which the nuclei as well as the electrons play their respective roles. It is further shown that the passage of X-rays through a crystal and their reflection by the stratifications of electron density can simultaneously result in vibrational energy transitions, provided that the modes of vibration thus excited involve displacements of electric charge and are therefore active as absorbers of infra-red radiation. Vibrational modes of this kind when excited result in periodic displacements of the stratifications of electron density. Consequently, reflections appear whose frequencies are less (or greater, as the case may be) than the frequency of the incident X-radiation. It is explained why it is possible for such reflections to appear even when the setting of the crystal is different from that required for the usual or unmodified reflections. The geometry of the X-ray reflections which then appear in displaced positions is also discussed.





## THE DIFFRACTION OF X-RAYS BY DIAMOND: PART II

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### 1. INTRODUCTION

FOR various reasons, diamond is the ideal case for a consideration of the consequences following from the ideas set out in Part I of this series of papers regarding the diffraction of X-rays by crystals. Since diamond is a cubic crystal of relatively simple structure, it is possible to determine and describe in purely geometrical terms the modes of vibration of which that structure is capable and with which we are concerned. It can also be shown that these modes have a high frequency, from which again it follows that they would not be thermally excited to any appreciable extent at ordinary temperatures. For the same reason also, it is permissible to ignore the disturbing effects on the phenomena with which we are concerned, of the thermal agitation in the crystal. It accordingly becomes possible to present a very clear picture of the effects which may be expected to present themselves to observation in strongly exposed X-ray diffraction patterns of diamond, on the basis of the theory developed in Part I.

### 2. THE STRUCTURE OF DIAMOND

Diamond exhibits in its structure a complete justification of Van't Hoff's hypothesis of the tetrahedral carbon atom. That hypothesis was originally put forward on the basis of the known chemical behaviour of carbon. It implies that the four valences which carbon exhibits in its compounds are tetrahedrally disposed in space and are indistinguishable from each other. Why this is so is one of the fundamental problems of theoretical chemistry. According to the spectroscopist's view of atomic structure, the nucleus of the carbon atom is surrounded by six electrons, two of which are in the inner or K-shell and the other four in the outer or L-shell. The latter four electrons again are assigned to two sub-groups, each containing two electrons. In the first sub-group, the electrons are assumed to be in the  $2s$  state, while the two electrons in the other sub-group are in the  $2p$  state. This situation of the four outer electrons is not in agreement with that indicated by the facts



of chemistry and hence it becomes necessary to modify the description of their states to bring it into line with the known chemical behaviour of carbon. All the four electrons have indeed to be considered as being in states indistinguishable from each other and so orientated that the resulting structure has perfect tetrahedral symmetry. Such a concept is necessary also to fit the picture of the carbon atom into the known facts concerning the structure of diamond. Having only two atoms in each unit cell, diamond nevertheless exhibits cubic symmetry. This situation requires that the nuclei of the carbon atoms occupy certain special positions in the crystal structure, namely, the points at which the four trigonal axes of cubic symmetry intersect each other.

The theory of hybridised orbitals is one of the best known attempts in the direction of describing the electronic state of the carbon atom in such manner as to bring it into line with the hypothesis of Van't Hoff. As full accounts of that theory are to be found in several recent treatises, it is not necessary here to expound it in detail. It is sufficient to mention that the states of the four electrons are assumed in that theory to be representable as a superposition of four hydrogen-like wave-functions which are so chosen that all the four electrons appear in similar states differing only in their orientations, which again exhibit tetrahedral symmetry. In the wave-functions assumed for the purpose, the  $2p$  states preponderate, and hence each of the four electrons is implicitly assumed to possess an orbital angular momentum about an axis which coincides in direction with its directed valence. We may remark that for the shell of valence electrons thus constituted to possess true tetrahedral symmetry, it is necessary that the orbital movements of the four electrons about their respective axes should be described in the same sense, that is to say, either all of them in a right-handed sense, or else all of them in a left-handed sense. We are thus led to recognize that there are two possible descriptions of the carbon atom, namely, a dextro-carbon atom and a lævo-carbon atom, which correspond respectively to the two possible senses of the orbital angular momentum of the electrons about the tetrahedral valence directions.

The considerations set forth above have important consequences in relation to the structure and physical properties of diamond. That crystal is usually described as made up of two non-equivalent sets of carbon atoms each located at the points of a face-centred cubic lattice; the two lattices interpenetrate each other in such manner that every carbon atom in one lattice is tetrahedrally surrounded by four others belonging to the other lattice. Accepting this description, it follows that in a truly homogeneous crystal of



diamond, only one out of four possible situations can exist: (i) both lattices are occupied by dextro-carbon atoms, (ii) both lattices are occupied by lævo-carbon atoms, (iii) one lattice is occupied by dextro-carbon atoms and other by lævo-carbon atoms, or (iv) the first lattice is occupied by lævo- and the second by dextro-carbon atoms. It is entirely possible that two or three or all four of these possible structures may exist simultaneously in different parts of the same crystal. It is sufficient, however, to consider here only the case of truly homogeneous diamonds the structure of which is exclusively one or another of the four categories set out above.

### 3. THE VIBRATION SPECTRUM OF DIAMOND

The vibration spectrum of a crystal containing  $p$  atomic nuclei in each unit cell consists of  $(24p - 3)$  distinct modes with monochromatic frequencies, supplemented by a continuous spectrum which is the residue representing the three omitted degrees of translatory freedom of motion. Since the unit cell of diamond contains 2 atomic nuclei only, we have 45 possible modes of vibration with monochromatic frequencies. The description of these modes and the evaluation of their frequencies have been very fully set out in an earlier memoir published in these *Proceedings*. In two other memoirs again, it has been shown that the heat capacity of diamond over the entire range of temperatures may be quantitatively evaluated in terms of these frequencies. It is therefore unnecessary to traverse the same field again, and indeed in the present paper we are only concerned with the three modes of vibration of highest frequency which may be described as an oscillation of the two lattices of carbon atoms with respect to each other along one or another of the three cubic axes. The free vibrations of the structure in all these three modes have the same frequency, and this is known exactly from spectroscopic studies on the diffusion of monochromatic light in diamond. A sharply defined line with a frequency shift of  $1332 \text{ cm.}^{-1}$  is recorded in the spectrum of the scattered light, and this frequency is associated with a vibration of the kind described above.

Whether the mode of vibration referred to above would be excited by the passage of X-rays through the crystal depends, as we have seen in Part I, on whether this mode is or is not active in the absorption of infra-red radiation. The circumstances which determine whether a specified mode of vibration in a crystal is active or not in the absorption of infra-red radiation have been considered by various authors and will be found discussed in detail in several recent treatises. It is a well-established rule deduced from theory and confirmed experimentally that if a structure possesses centres of symmetry,



any mode of vibration which manifests itself as a frequency shift in light scattering would be *inactive* in the absorption of infra-red radiation. In the first two sub-species of diamond referred to above, both sets of carbon atoms are dextro-carbon atoms or both lævo-carbon atoms respectively. It is clear that every point midway between a pair of atoms belonging respectively to the two lattices would in these cases be a centre of symmetry. Accordingly, in these two sub-species of diamond, since the mode of vibration with the frequency  $1332\text{ cm.}^{-1}$  manifests itself as a frequency in light-scattering, that mode would be *inactive* in infra-red absorption. *Per contra*, in the two other sub-species of diamond where the carbon atoms located at the points of the two lattices are of different species, the points midway between two carbon atoms are *not* centres of symmetry. Hence the rule of mutual exclusion stated above is not applicable in their cases and hence the modes of vibration would be active *both* in the scattering of light and in the absorption of infra-red radiation. In what follows, we shall refer to the first two sub-species of diamond as the Oh I and Oh II types of diamond respectively, and the two other sub-species as Td I and Td II respectively. The use of these symbols has a special significance, *viz.*, that the electronic structure of the first two species of diamond has the full or octahedral symmetry of the cubic system; whereas the electronic structure of the two other species has only the lower or tetrahedral symmetry.

We may conclude this section by a categorical statement of the results indicated by the theory. *In diamonds which belong to the two sub-species Oh I and Oh II, the fundamental vibration of the structure with frequency of  $1332\text{ cm.}^{-1}$  would not be active in infra-red absorption and hence the passage of X-rays through the crystal would not excite that vibration and hence would not result in a dynamic reflection. Per contra, in diamonds which belong to the two other sub-species Td I and Td II, the said vibration would be active in the absorption of infra-red radiation and hence the passage of X-rays through the crystal would excite those vibrations and give rise to dynamic reflections by the lattice planes in the crystal.*

#### 4. THE PHASE WAVES OF DYNAMIC REFLECTION

We shall proceed to consider the nature of the dynamic reflections which may be expected to manifest themselves in the case of diamonds possessing only the lower or tetrahedral symmetry of electronic structure as the result of the excitation of the infra-red active vibration. As already stated, this vibration is an oscillation of the interpenetrating lattices of carbon atoms (in these cases dissimilar to each other) along one or another of the three cubic axes of the crystal. The atoms belonging to the two lattices appear in distinct but



equidistant layers parallel to the cubic planes. The infra-red activity of the vibration arises from the fact that the electronic structure of the carbon atoms in the alternate layers is not completely identical. Hence, the oscillations of the two lattices with respect to each other results in periodic displacements of electric charge along the direction of vibration. We have three such movements to consider, which are respectively along one or another of the three cubic axes of the crystal. Hence, we have also three sets of phase-waves to consider whose normals are likewise the cubic axes.

The oscillatory movements of electric charge along the cubic axes of the crystal would necessarily also result in periodic movements of the stratifications of electric charge which appear in the crystal in other directions. In considering the question whether these movements would give rise to dynamic reflections by those stratifications, we have to remark that movements *parallel* to any set of stratifications cannot give rise to any dynamic reflections by them; only movements *normal* to the stratifications can give rise to such reflections, and hence if the actual movements are *inclined* to the stratifications, we need consider only the components of the movement along their normals.

Considering for example the (111) planes in a crystal, the three movements respectively along the three cubic axes are equally inclined to those planes, and hence the magnitude of all the three components resolved along the normal to the (111) planes would be diminished to the same extent. Hence, in general, *the (111) planes would give three dynamic reflections* which in appropriate circumstances, may be expected to be of comparable intensities. On the other hand, the (220) planes of the crystal contain one cubic axis and are equally inclined to the other two at angles of  $45^\circ$ . The displacements of electric charge parallel to the first axis and hence also parallel to the plane of the stratifications would not give rise to any dynamic reflection. However, movements along the two other cubic axes would result in a displacement of the stratifications in the (220) planes diminished to equal extents by reason of their inclination to those planes. We conclude that *the (220) planes would give only two dynamic reflections* which in appropriate circumstances would be of equal intensity. Considering again the (400) planes, these contain two of the cubic axes and are normal to the third, it follows for similar reasons that *the (400) planes give only one dynamic reflection*. The fact that the phase-waves are parallel to those planes has a further interesting consequence to which we shall revert later. Finally, we may briefly consider the (311) planes. These planes are equally inclined to two of the cubic axes at small angles and are nearly perpendicular to the third. The dynamic

reflections due to the first two movements may therefore be expected to behave very differently from the third.

### 5. THE GEOMETRY OF THE DYNAMIC REFLECTIONS

The general method already indicated in Part I enables us to picture the configuration of the dynamic reflections given by the various lattice planes in the crystal. We shall here content ourselves with the consideration of the dynamic reflections associated with the (111), (220), (311) and (400) planes, since these are the four largest spacings in the crystal which also reflect X-rays with notable intensity. The first three cases are represented in Figs. 1, 2 and 3 respectively for settings of the crystal so chosen that the

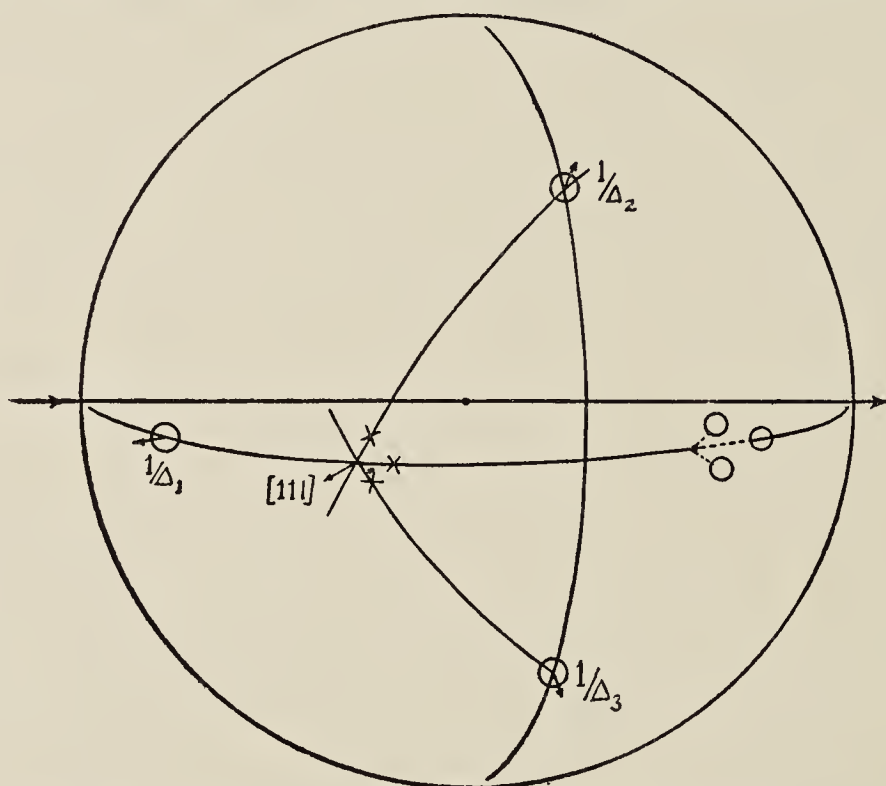


FIG. 1. Dynamic Reflections by the (111) planes.

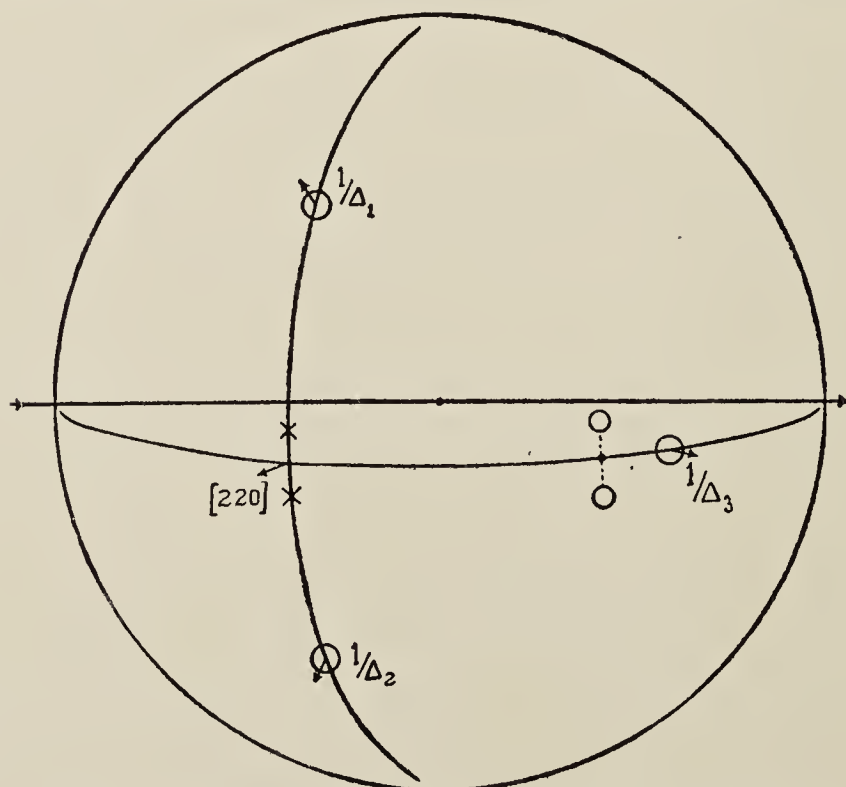


FIG. 2. Dynamic Reflections by the (220) planes.



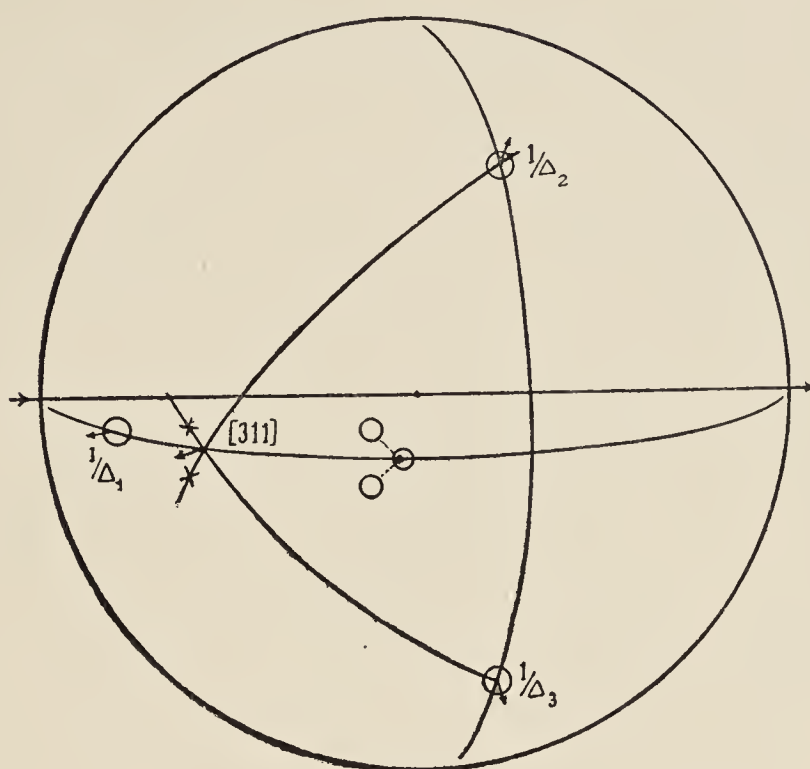


FIG. 3. Dynamic Reflections by the (311) planes.

characteristic features of each case are brought out clearly. The primary X-ray beam is assumed to traverse the crystal horizontally and its direction is indicated by arrows at the points of entry and exit on a sphere. The plane of incidence on the lattice-spacings is also assumed to be horizontal and is indicated by a great circle drawn on the surface of the sphere. The normal to the lattice spacings accordingly appears as a point on the same great circle with an arrow attached to it and directed radially outwards. The three cubic axes of the crystal which are the normals to the phase-waves of dynamic reflection are represented on the sphere in a similar fashion, the points where they appear being determined by the chosen setting of the crystal. Three great circles are also drawn each of which contains one of the phase-wave normals and the normal to the lattice spacings. In each case the setting of the crystal chosen is such that one of the great circles coincides with the plane of incidence. The normals to the three sets of dynamic stratifications would necessarily lie on these three great circles. The positions of the dynamic reflections would be determined by drawing three other great circles, each containing the direction of the incident beam and the normal to the particular dynamic stratification, and marking off on these circles, points such that the angle of reflection is equal to the angle of incidence in the respective planes. The entire procedure is that indicated by the theory of dynamic reflection developed in Part I and contained in the two equations

$$\frac{\vec{1}}{D} = \frac{\vec{1}}{d} + \frac{\vec{1}}{\Delta} \quad (1)$$

$$2D \sin \psi = \lambda \quad (2)$$

For a particular X-ray wavelength determined by the lattice spacings and the angle of incidence of the X-rays on them, we would observe the ordinary or unmodified reflection in the plane of incidence. The direction in which this appears is represented in each of the figures as another point on the equatorial circle. For the same X-ray wavelength, the dynamic reflection or reflections permitted would also appear in the same direction superposed on the ordinary or static reflection. For other X-ray wavelengths, the static reflection ceases to appear but the dynamic reflections would persist, their directions being determinable in the manner already explained. The phase wavelength is infinite for the particular case in which the static and dynamic reflections are superposed. With progressively changing X-ray wavelength,  $1/\Delta$  would increase in numerical magnitude and the point on the sphere representing the dynamic stratification would move out in one direction or another along the great circle which defines its path. The construction already indicated would then result in giving positions to the dynamic reflections differing from that in which they were originally coincident. In the particular settings of the crystal which have been chosen for drawing the figures, the dynamic reflection which corresponds to the cubic axis in the plane of incidence would—if it exists at all—appear in the plane of incidence, while the other two would swing out of that plane symmetrically in either side.

For reasons already explained, whereas the (111) planes show *three* dynamic reflections in the setting indicated, the (220) planes show only two reflections: these are displaced laterally, one on either side. The third reflection lying in the plane of incidence though *geometrically* permitted is *physically* excluded by reason of the movement of the stratifications being in their own plane. The case of (400) reflection is of special interest. As explained earlier, only one dynamic reflection is possible in this case and since the phase-waves which give that reflection are parallel to the stratifications themselves, the dynamic reflection for all X-ray wavelengths would appear in the same direction, *viz.*, that indicated by the ordinary law of geometric reflection.

## 6. SUMMARY

Considerations of the physical nature of the directed valences of the tetrahedral carbon atom lead to the conclusion that there are two possible states of the carbon atom, *viz.*, a dextro-state and a lævo-state corresponding respectively to the two possible senses of the orbital angular momentum of the electrons about their tetrahedral valence directions. From this again it follows that a homogeneous diamond crystal may have an electronic structure which has either the highest or octahedral symmetry or else only the lower



or tetrahedral symmetry of the cubic system. In diamonds having octahedral symmetry, the oscillations of the two carbon atoms with respect to each other would be inactive in the absorption of infra-red radiation, whereas in diamonds of which the electronic configuration has tetrahedral symmetry that vibration would be active in such absorption. From this it follows that only with diamonds of the latter type would the X-rays excite the lattice vibrations and exhibit the dynamic reflections consequent thereon. The vibrations excited and their phase-wave-normals are parallel to the three cubic axes of the crystal. It follows that whereas the (111) planes would exhibit *three* dynamic reflections at any one setting of the crystal, the (220) would exhibit only *two* and the (400) planes only *one*.





## THE DIFFRACTION OF X-RAYS BY DIAMOND: PART III

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### 1. INTRODUCTION

IN the first part of the present memoir, it was shown from theoretical considerations of a very general nature that when X-radiations traverse a crystal, their passage could result in exciting vibrational transitions in the energy levels of the crystal and as a consequence of such excitation lead to a reflection of the incident X-rays by the lattice planes of the crystal with a change of frequency. The theory indicated it as an essential condition for such a process to occur that the vibrational transitions in question are effective as absorbers of infra-red radiation of the appropriate frequency. The phenomenon here envisaged is quantum-mechanical in its nature; in other words, vibrational transitions would be excited and would be accompanied by X-ray reflections of altered frequency even when the frequency of the vibrations is so high that they would not be thermally excited to any appreciable extent. However, considerations of a purely classical nature assist in elucidating the nature of the phenomenon and in deducing its observable features. The infra-red activity of a vibrational mode in a crystal arises because it involves a periodic displacement of the electronic clouds in the crystal with the same frequency; such a displacement would result in an oscillation of the stratifications of electron density which reflect the X-rays traversing the crystal and hence also to dynamic reflections of altered frequency.

Perhaps the most striking feature of the theory expounded in Part I is the connection which it indicates between the behaviour of a crystal in X-ray diffraction and the activity of the modes of its internal vibration in the absorption of infra-red radiation. The particular case of diamond is of special interest in this connection. For, as was shown in Part II of the memoir, theoretical considerations indicate that diamonds should be forthcoming in forms which differ in the inner symmetry of their electronic configuration and hence also in their infra-red behaviour. The detailed discussion showed that the diamonds of which the inner symmetry is octahedral would *not* exhibit dynamic X-ray reflections, whereas those diamonds of which the



symmetry is tetrahedral would exhibit such reflections. In other words, the case of diamond enables us to put the relation between X-ray diffraction and infra-red activity to a direct experimental test. Further, it was also shown in Part II of the memoir that in the case of diamond, we are concerned with three modes of vibration which are respectively parallel to the three cubic axes of crystal and hence variously inclined to the lattice-spacings in it. As a result, the dynamic reflections by these spacings differ both in their number and in their geometric configuration in a highly characteristic fashion. Thus, the application of the general theory to the particular case of diamond furnishes us with abundant material for comparison with the facts of experiment.

## 2. THE TETRAHEDRAL AND OCTAHEDRAL FORMS OF DIAMOND

Three diamonds employed in the present investigation are represented in Plate I. The first is a cleavage plate parallel to the (111) spacings of the crystal. The second is a flat tabular crystal in its natural form as a hexagonal plate with faces parallel to the (111) planes. The third is a thin faceted plate of diamond with its faces nearly parallel to the (111) planes. All three diamonds are perfectly colourless, without any visible cracks or inclusions in their interior and obviously of the highest quality. Nevertheless, the first two diamonds differ enormously in their physical behaviour from the third, as is apparent from a comparison of the photographs reproduced in the Plate. We proceed to explain how these photographs were obtained.

The photographs on the left-hand side were recorded by placing the diamond against a fluorescent screen. (This was a slab of lithium fluoride crystal impregnated with a little uranium oxide.) The  $\lambda$  2537 radiation from a water cooled magnet-controlled mercury arc in quartz was isolated by a monochromator and allowed to fall on the diamond and then on the LiF-UO<sub>2</sub> screen placed behind it, and the fluorescence excited in the latter was photographed from the rear. The photographs on the right-hand side of the Plate were obtained in a very simple manner. The diamond was placed between two crossed polaroids and photographed as seen through them against a bright source of light. It is seen from the photographs reproduced in Plate I that *the cleavage plate and the tabular crystal are both perfectly opaque to the  $\lambda$  2537 radiations of the mercury arc and that they exhibit not a trace of birefringence, in other words that they are truly and perfectly isotropic crystals.* On the other hand, *the thin faceted plate is completely transparent to the  $\lambda$  2537 radiations of the mercury arc, but it exhibits a feeble but nevertheless readily observable birefringence pattern with definite geometric features related in their orientation to the structure of the crystal.*



Diamond is, in effect, a giant macro-molecule of carbon. Hence a specimen of it which exhibits no detectable birefringence, in other words, is optically homogeneous, may, *prima facie*, be expected to make a close approach to the ideal state of crystal perfection. *Per contra*, a specimen of diamond—which exhibits over its entire area, a geometric pattern of birefringence however feeble it may be in intensity—must necessarily be regarded as very remote from such ideality. A striking confirmation of the correctness of these remarks is furnished by the results of a simple experimental test in which the diamonds figured in Plate I were used as X-ray spectrometers to resolve the  $K\alpha_1$  and  $K\alpha_2$  radiations from a copper target. The X-ray beam from the target diverged through a fine slit and fell on the diamond in an appropriate setting placed at a distance of 5 cm. from the slit. The surface reflection of the X-rays by the (111) planes of the crystal was recorded on a photographic film held at a distance of about 100 cm. The spectrograms recorded with the flat tabular diamond and by the faceted plate are reproduced as Fig. 1 (a) and 1 (b) respectively in Plate II. A very great difference between the two diamonds in regard to the degree of their crystal perfection is indicated by the difference in the two spectrograms. But the actual difference is even greater. For, the width of the  $K\alpha_1$  and  $K\alpha_2$  lines as recorded in Fig. 1 (a) in Plate II represents the natural spectral widths of these radiations and is therefore not a true measure of the crystal perfection of the tabular diamond. To obtain a true measure of that perfection, it is necessary to adopt a spectrographic technique in which two crystals of diamond are employed. The results of that technique are depicted in the series of spectrograms reproduced as Fig. 2 (a), (b), (c) and (d) of Plate II and in Figs. 1 (a), (b) and (c) of Plate X. We shall revert to the details of the technique and the significance of the results obtained with it in a subsequent section of the present paper.

Studies on the infra-red absorption spectra of diamond have established the fact that diamonds which are completely transparent to the  $\lambda$  2537 radiations of the mercury arc in the ultra-violet are also completely transparent to infra-red radiations over the entire range of the characteristic frequencies of vibration of the structure of diamond ranging from  $1332\text{ cm.}^{-1}$  downwards to longer wavelengths. *Per contra*, the diamonds which are opaque to the  $\lambda$  2537 radiations also exhibit a marked absorption over that entire range of infra-red wavelengths. It is thereby established that diamonds of the former kind possess an inner electronic configuration which has the full or octahedral symmetry of the cubic system, whereas the diamonds of the latter kind possess an electronic configuration which possesses the lower or tetrahedral symmetry of that system. The remarkable fact that diamonds with



a lower degree of symmetry are highly perfect crystals, while those with a higher degree of symmetry are highly imperfect receives a natural explanation on the basis of the theory of the structure of diamond expounded in Part II of the memoir. As there explained, the tetrahedral diamonds are those in which each dextro-carbon atom is linked to four lævo-carbon atoms and likewise each lævo-carbon atom is linked to four dextro-carbon atoms. *There is thus no physical difference between the two sub-species Td I and Td II* of the tetrahedral class of diamonds but only an interchange in the description of the two lattices which constitute the structure. On the other hand, the octahedral type of diamonds consists entirely of dextro-carbon atoms or entirely of lævo-carbon atoms; *the two sub-species Oh I and Oh II are therefore physically different*. These circumstances are clearly favourable for the Td diamonds exhibiting a high degree of homogeneity and for the Oh diamonds to be markedly heterogeneous in their texture. But there is another and a deeper consideration which has also to be borne in mind. When a dextro-carbon atom is linked to a lævo-carbon or *vice versa*, the two electrons shared between them describe their orbits about the valence direction in the same sense. On the other hand, when a dextro-carbon atom combines with a dextro-carbon atom or a lævo-carbon atom with a lævo-carbon atom, the shared electrons describe their orbits about the common valence direction in opposite senses. It would seem that a homogeneous structure extending through large volumes would be more likely to appear in the former case than in the latter.

It is appropriate at this stage to remark that it is the perfect diamonds belonging to the tetrahedral class that exhibit the phenomena of dynamic reflection of X-rays, while it is the imperfect diamonds of the octahedral type that do not show those phenomena. This is in agreement with the indications of the theory developed in Part II of the memoir. But it is necessary to demonstrate that the failure of the octahedral diamonds to exhibit dynamic reflections is not ascribable to their imperfection of structure, but is a consequence of their inactivity in infra-red absorption. We shall revert to this presently.

### 3. DYNAMIC X-RAY REFLECTIONS AND CRYSTAL SYMMETRY

Figure 1 in Plate III is a Laue photograph of a cleavage plate of diamond whose faces are parallel to the (111) planes of the crystal. The crystal was set exactly normal to a fine pencil of X-rays from a copper target. The picture shows perfect trigonal symmetry not only with regard to the ordinary or Laue reflections but equally also with regard to the dynamic reflections appearing in the vicinity of the hexagonal corners of the print adjacent to



the intense (111) Laue spots. Figure 2 in Plate III is a similar photograph taken in similar circumstances with a crystal of diamond which exhibits twinning of the spinel type. It will be seen that this pattern exhibits hexagonal symmetry in all its features, including especially the dynamic reflections which are seen at all the six corners of the hexagonal print. The fact clearly evident from Figs. 1 and 2 in Plate III that the dynamic X-ray reflections of diamond exhibit the symmetry of the crystal in the same manner and to the same extent as the static reflections is obviously of the highest significance. Taken in conjunction with the circumstance that the diamonds which exhibit the dynamic reflections are perfect and indeed—as will appear presently—are ideal crystals, it demonstrates the correctness of the view expressed by the author in the original publication of the year 1940 that these phenomena exhibited by diamond are fundamental in their nature and of the highest importance in relation to the theory of X-ray diffraction in crystals.

As already remarked earlier, the fact that the dynamic reflections are not manifested by the diamonds of octahedral symmetry is a confirmation of the theoretical ideas set out in Part I of the memoir. But the circumstance that these diamonds are imperfect tends to create some doubt in the matter. Very frequently, indeed, diamonds of this class give distorted Laue patterns. Hence a critical observer might be disposed to infer that it is this imperfection rather than the inactivity in infra-red absorption which is responsible for the non-appearance of the dynamic reflections. To dispel such an impression, it is necessary to investigate the matter with carefully selected material. The intensity of the birefringence exhibited by these diamonds is a measure of the imperfections in their structure. It is therefore desirable to select a specimen in which such birefringence is of extremely low intensity. The specimen illustrated in Figs. 3 (*a*) and 3 (*b*) in Plate I was found to be the best available in this respect. Even so, the mosaicity of its structure exhibits itself in a notable enhancement of the intensity of the Laue spots in its diffraction patterns. Such enhancement is particularly striking in the case of spots that are only feebly recorded with diamonds of the tetrahedral class. Even such a weak effect as the diffuse X-ray scattering due to thermal agitation is recorded with greatly enhanced intensity by this specimen. But there is no observable distortion of the Laue spots, and had the dynamic reflections been present, they would have been very striking features in the recorded patterns. Actually, not a trace of them is observable in Figs. 1 (*b*) and 1 (*d*) in Plate VIII which were recorded with this diamond in appropriate settings. For the sake of comparison, the patterns recorded with the tetrahedral diamond in identical settings are reproduced as Fig. 1 (*a*) and 1 (*c*) side by side with them in the same Plate VIII.



## 4. OBSERVABLE FEATURES OF THE DYNAMIC REFLECTIONS

The following special points are worthy of mention:

- I. As the dynamic reflections by diamond are a consequence of the excitation by the incident X-rays of an infra-red vibration of high frequency, variations of temperature within wide limits should be entirely without effect either on the intensity or the sharpness of these reflections.
- II. As a result of the crystal perfection of diamond, the ordinary reflections of monochromatic X-rays would demand a very precise setting of the crystal for their observation, on either side of which they would disappear completely. The dynamic reflections would coincide with the static reflections at the correct setting, but would not disappear when the setting is altered. Their intensity would however fall off rapidly as the crystal is moved away from the correct setting in their direction.
- III. The dynamics of the excited vibration in diamond demands that the phase-waves which determine the direction in which the dynamic reflections appear are precisely normal to one or another of the cubic axes of the crystal. As a consequence, the reflections would be very sharply defined, being indeed in this respect almost comparable with the static reflections.
- IV. By making observations of the directions in which the dynamic reflections appear, it is possible to determine the orientation of the phase-waves. The most suitable arrangement for such determination is to place the crystal so that one of the cubic axes lies in the plane of incidence of the X-rays on the (111) planes, and then to alter the setting in such manner that the plane of incidence does not change. The geometric law of dynamic reflection takes a very simple form in this case and a precise measurement of the orientation of the phase-waves becomes possible.

The various special features referred to above were all fully established by the observations made by the author and his collaborators in the months following the original publication of April 1940. Detailed reports of those studies appeared in the *Proceedings of the Indian Academy of Sciences* in the years 1940 and 1941. It would be superfluous here to traverse the same ground or to comment on the literature of a controversial nature published from other laboratories on the subject then and subsequently. To



make the present memoir complete, however, a series of photographs showing the dynamic reflections by the (111) planes, (220) planes, (311) planes and (400) planes of diamond in various settings are reproduced as Plates IV, V, VI, VII, VIII and IX accompanying the present paper. A comparison of the features noticed in this series of photographs with the theoretical diagrams given in Part II of the memoir will show how complete the agreement is between fact and theory.

### 5. SPECTRAL ANALYSIS OF X-RAY DIFFRACTION

We now return to a detailed description of the technique which enables a spectroscopic analysis to be made of the X-ray diffraction phenomena exhibited by diamond. The general nature of this technique to which a brief reference was made earlier will be evident from Fig. 1, text. A powerful source of X-rays from a copper target passes first through a wide slit and then

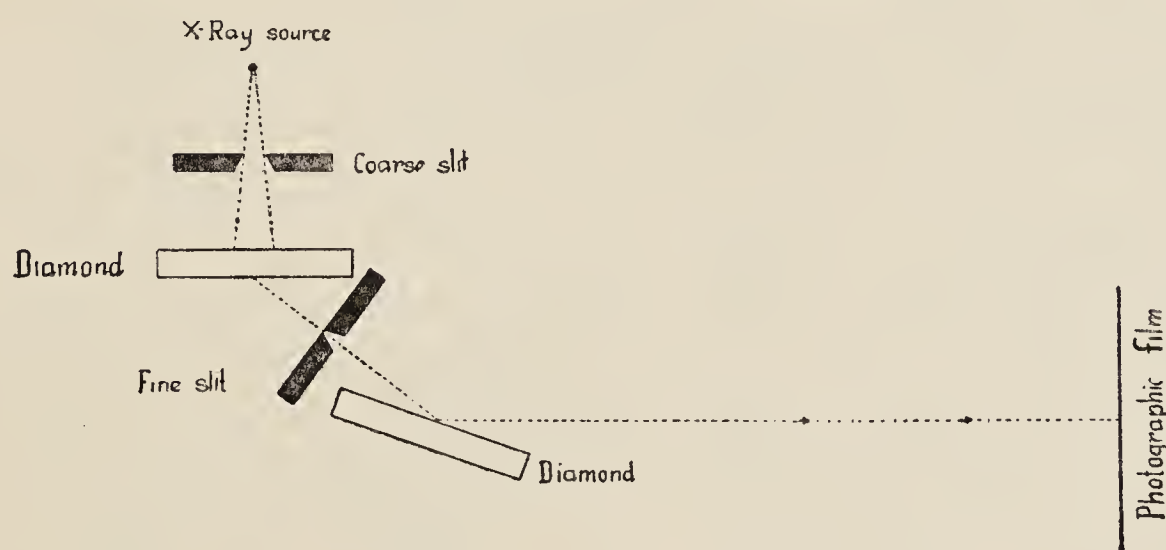


FIG. 1 (Text)

through the diamond under study. The rays *internally* diffracted by the (111) planes of this diamond are restricted by a fine slit through which they pass before they are incident on the surface of a second perfect diamond which functions as a spectrometer. The rays reflected *externally* by the second diamond are received and recorded on a photographic film placed at a distance of 100 cm. The actual technique consists in rotating the first diamond in steps through very small angles over a total range of a few minutes of arc. What is actually recorded on the photographic film is the spectrum of X-radiation in the narrow range between the  $K\alpha_1$  and  $K\alpha_2$  lines and perhaps a little more on either side of them.

The nature of the results obtained will be evident from a scrutiny of the series of spectrograms reproduced as Figs. 2 (a), (b), (c) and (d) in Plate II and the three others which appear as Fig. 1 (a), (b) and (c) in Plate X. The latter three have been enlarged so as to be readily comparable with the single

crystal spectrogram appearing as Fig. 1 (*a*) in Plate II. The most significant feature of the series of spectrograms is the appearance of an extremely sharp line which drifts in its position as the diamond is rotated. The spectral width of this sharp line is not more than about a tenth of the natural width of the  $K\alpha_1$  or the  $K\alpha_2$  radiations. It represents the super-monochromatic radiation manufactured by the first diamond from the incident white radiation by Laue reflections at the (111) stratifications. Its extreme sharpness reflects the extraordinary perfection of the diamond.

It will be seen that the relative intensities of the  $K\alpha_1$  and  $K\alpha_2$  lines differ enormously in the different spectrograms. That they persist over the whole range of settings of the diamond clearly shows that they represent the dynamic reflections of the  $K\alpha_1$  and the  $K\alpha_2$  radiations by the (111) planes of the first diamond. The static reflections of those radiations are recorded only at the precise settings at which those reflections are possible.

#### 6. ACKNOWLEDGEMENT

The Laue patterns reproduced in Plates III, IV, V, VI, VII, VIII and IX, as well as the single crystal and double crystal X-ray spectra reproduced in Plates II and X accompanying this memoir were recorded in the X-ray Laboratory of the Raman Research Institute by the Assistant Director of the Institute, Professor A. Jayaraman, for whose valuable co-operation in the research the author of this memoir is greatly indebted. The gift to the Institute of a rotating target X-ray set by Sir Purushottamdas Thakurdas made the work possible.

#### 7. SUMMARY

Studies on the crystal perfection of diamond by single-crystal and the double-crystal X-ray spectroscopic methods demonstrate that the non-birefringent diamonds which are infra-red active and possess only tetrahedral symmetry in their electronic configuration are extraordinarily perfect and are indeed ideal diamonds. It is these diamonds that exhibit the phenomena of dynamic reflection of X-rays. The detailed studies of the phenomena show that the experimental facts of the subject are completely in agreement with the results of the theory expounded in the first two parts of the memoir. The non-appearance of the dynamic X-ray reflections with the diamonds which have an octahedral symmetry of electronic configuration is shown to be consequential on these diamonds being inactive in the absorption of infra-red radiation.



FIG. 1 (a)



(b)

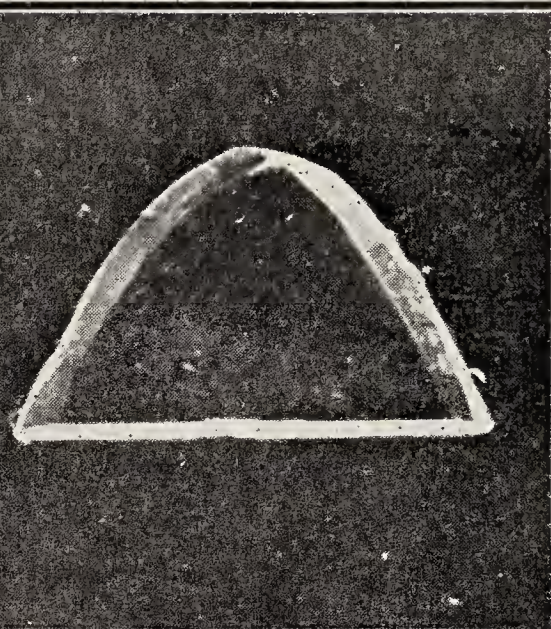
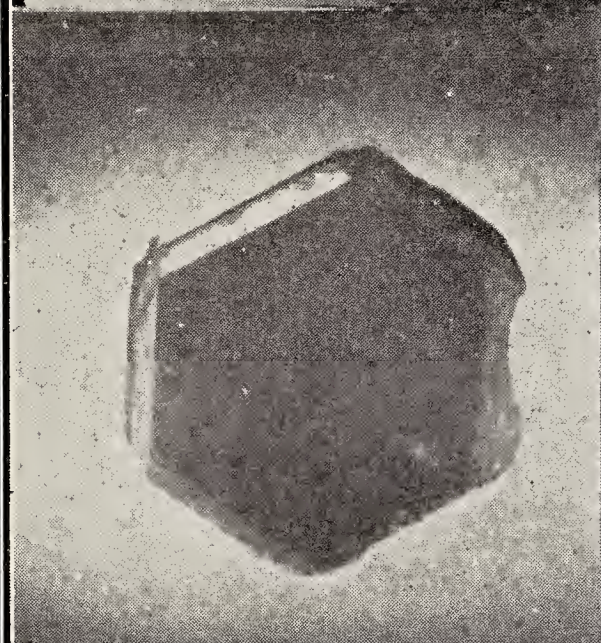


FIG. 2 (a)



(b)

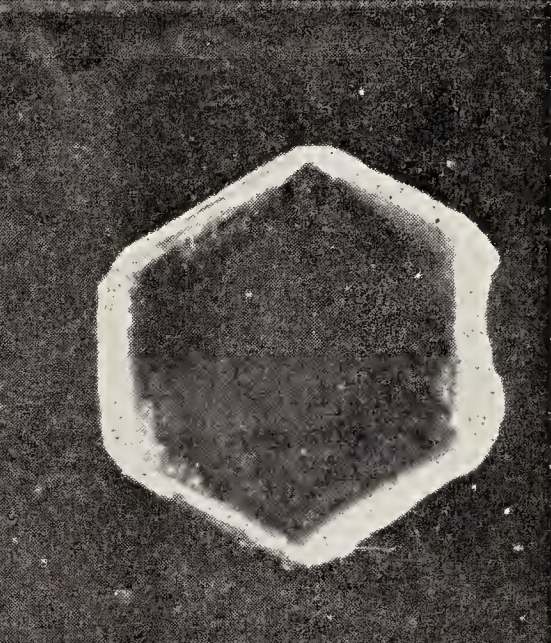
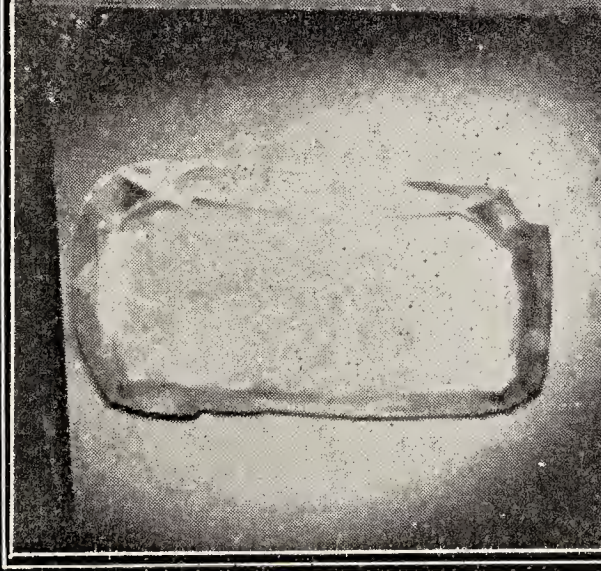


FIG. 3 (a)



(b)

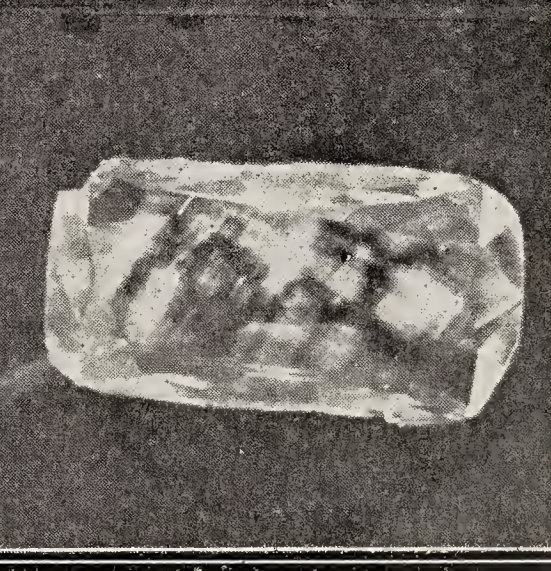
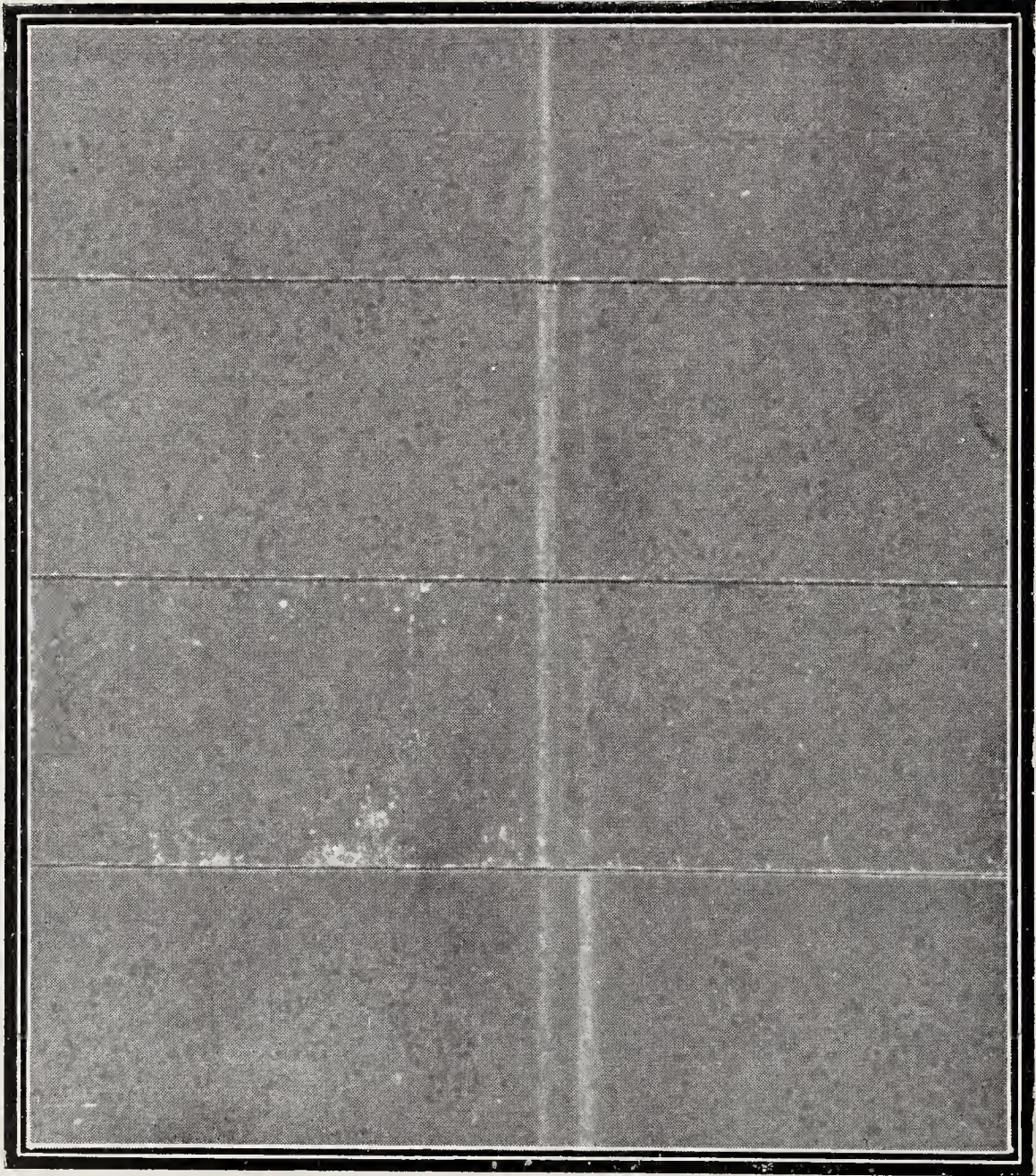
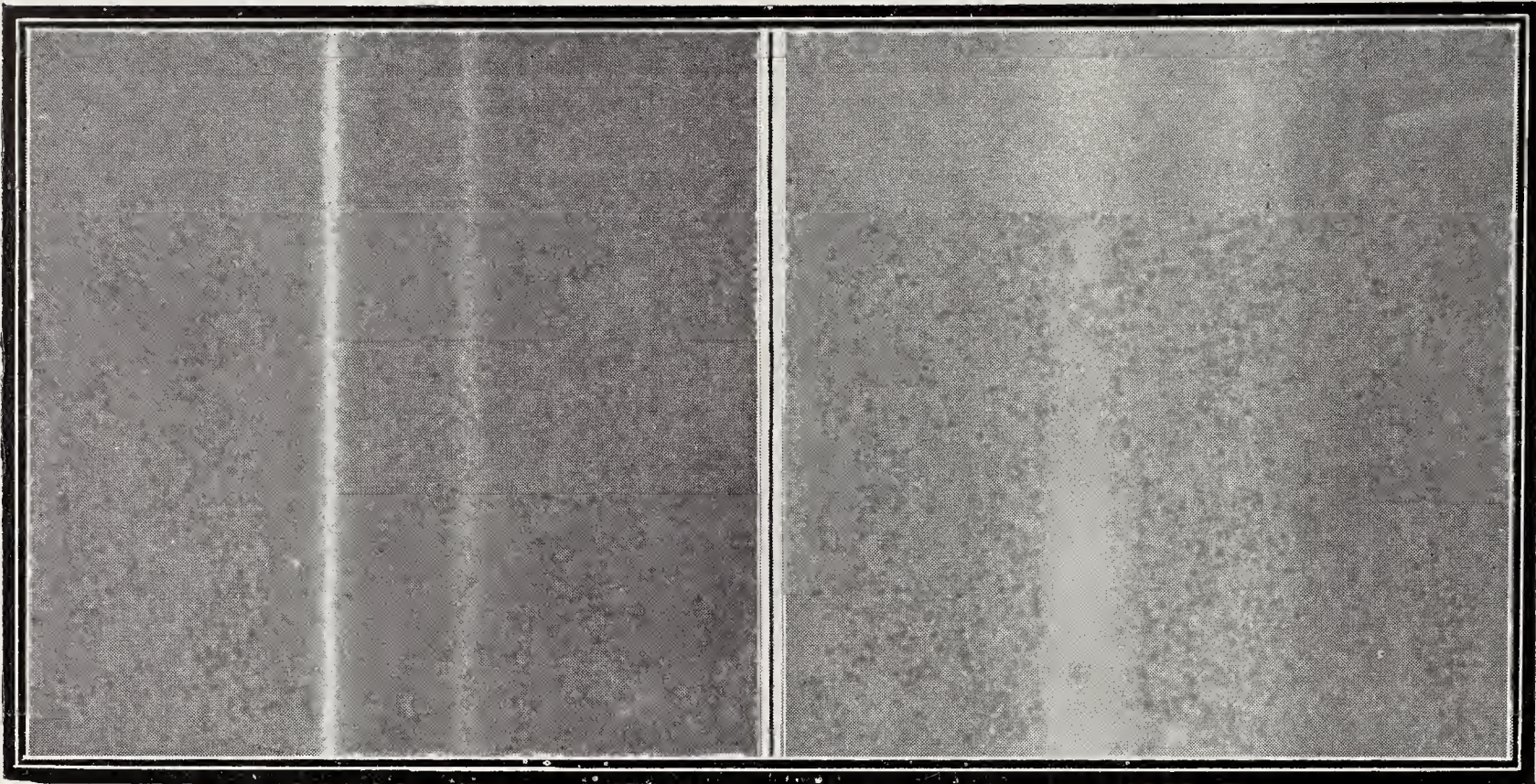




FIG. 1 (a)

FIG. 1 (b)



(a)

(b)

(c)

(d)

FIG. 2



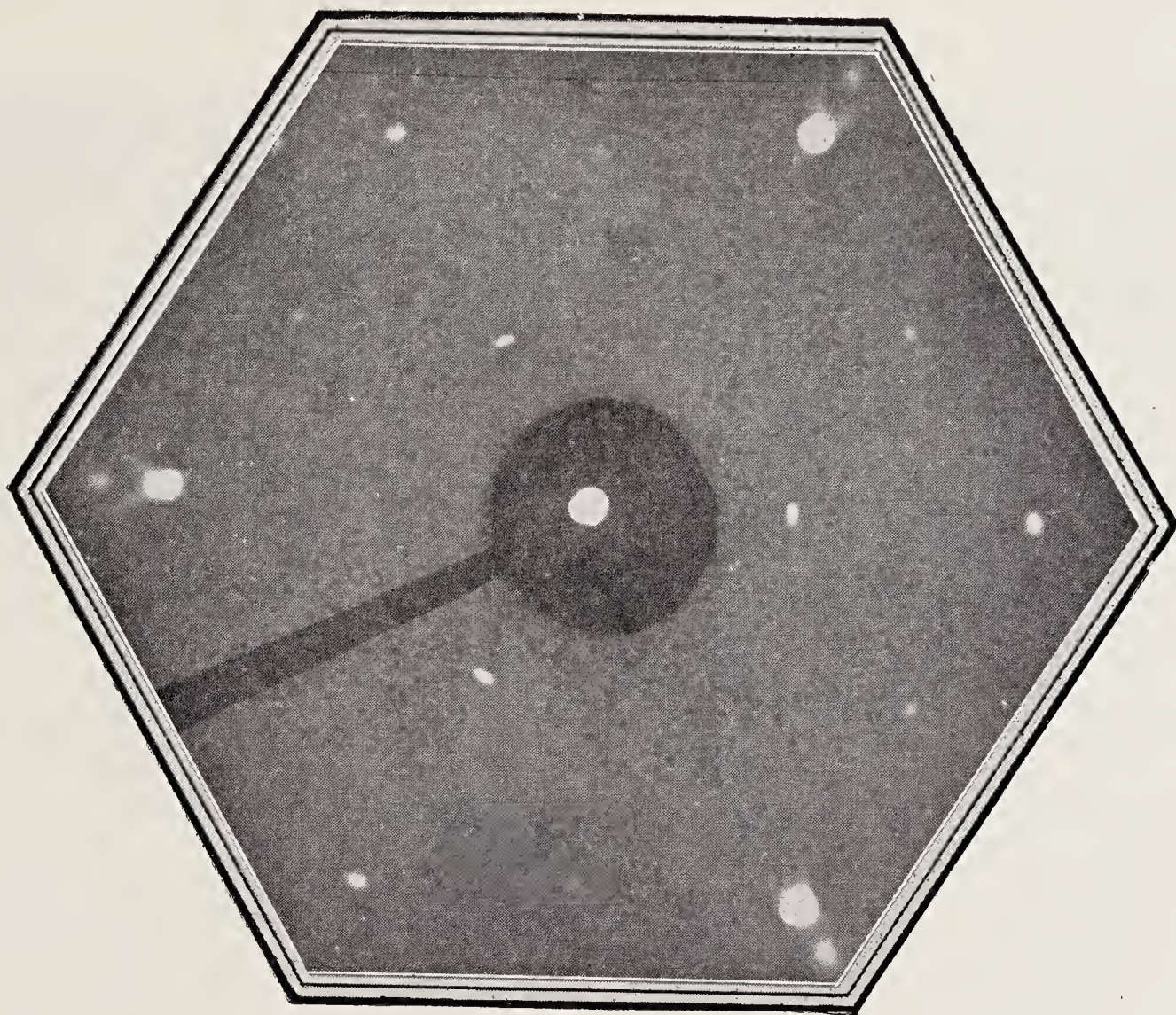


FIG. 1

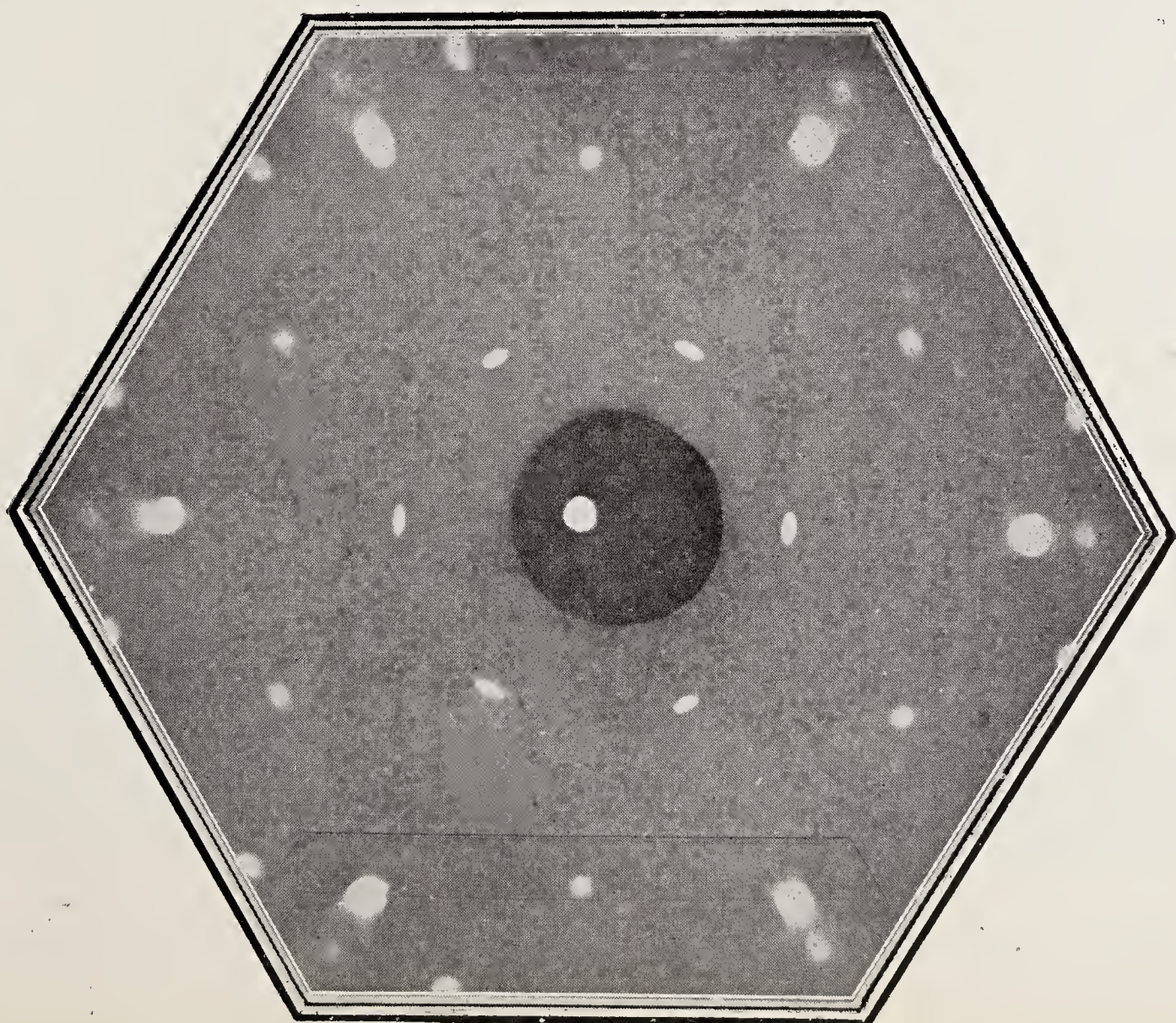


FIG. 2



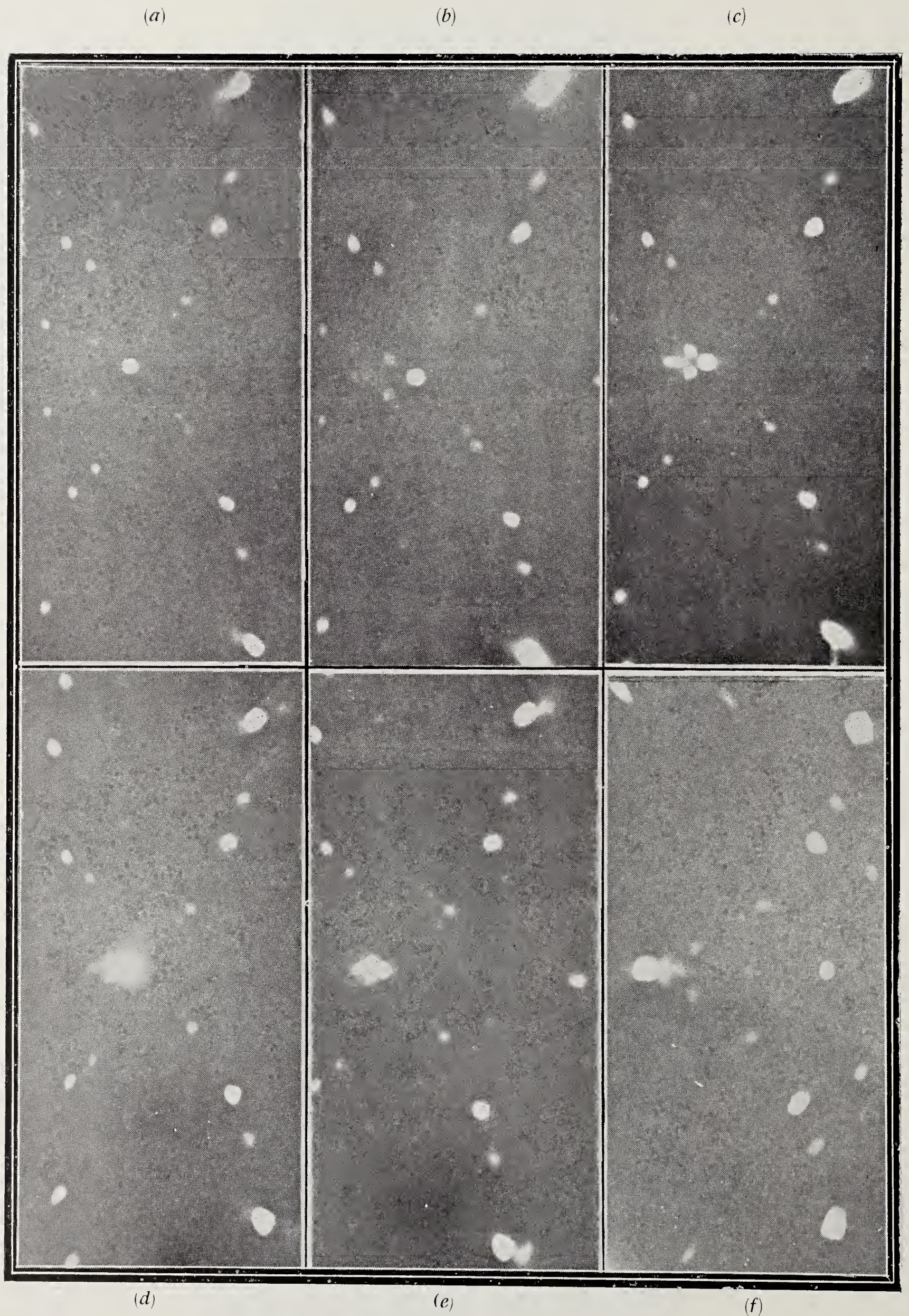


FIG. 1. Exhibiting the dynamic reflections by the (111) planes at various settings.



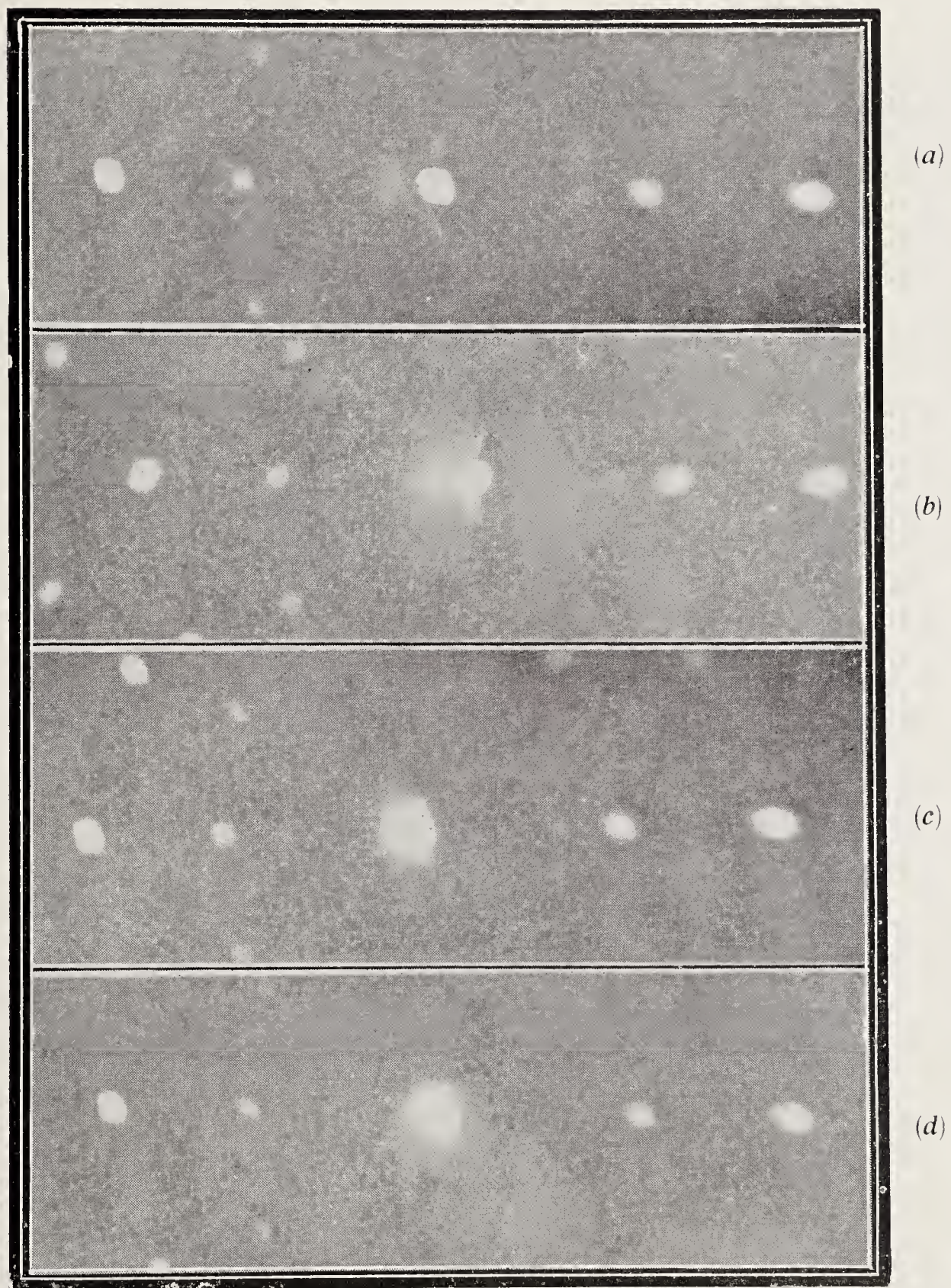


FIG. 1. Exhibiting the dynamic reflections by the (220) planes at various settings.



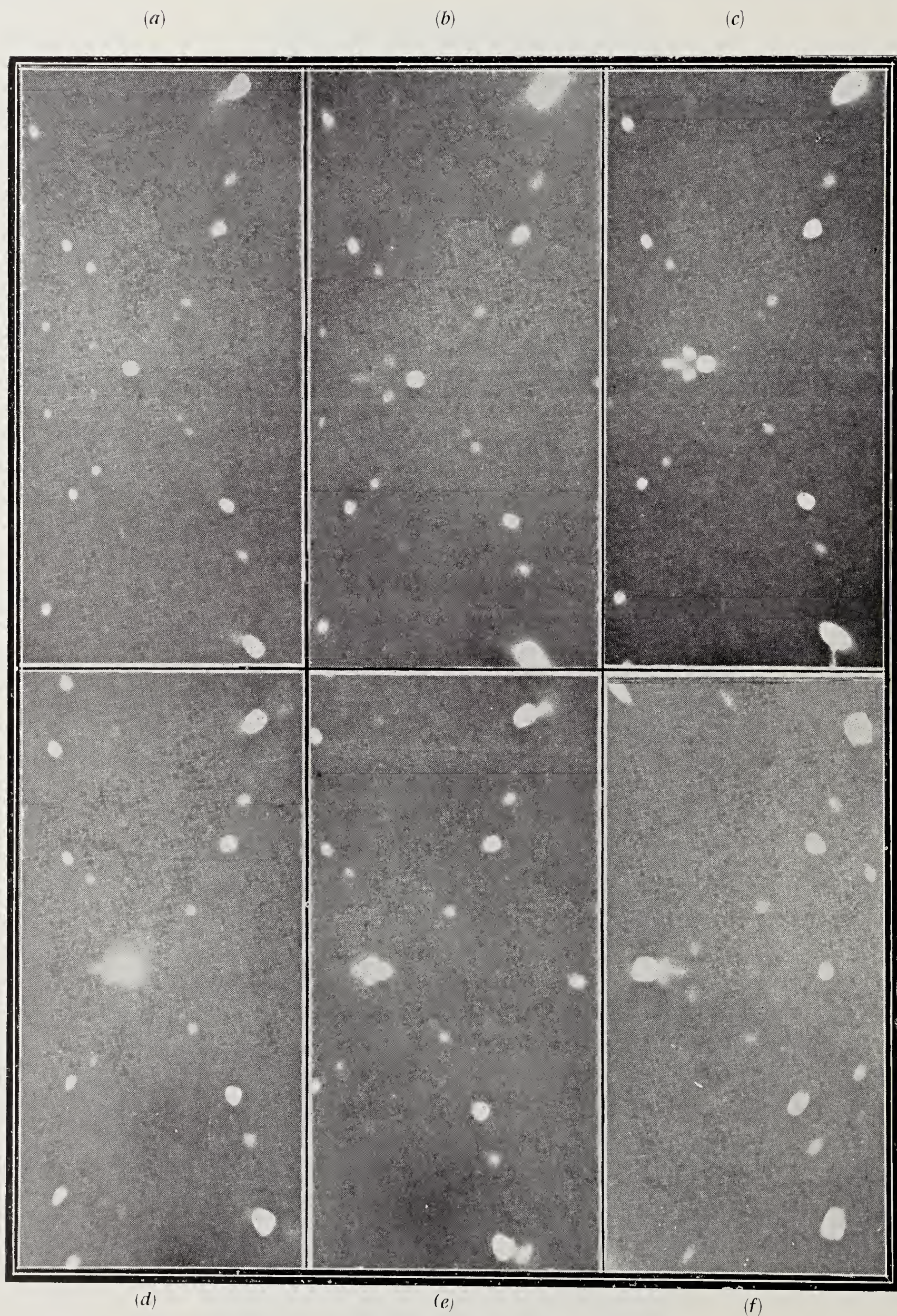


FIG. 1. Exhibiting the dynamic reflections by the (111) planes at various settings.



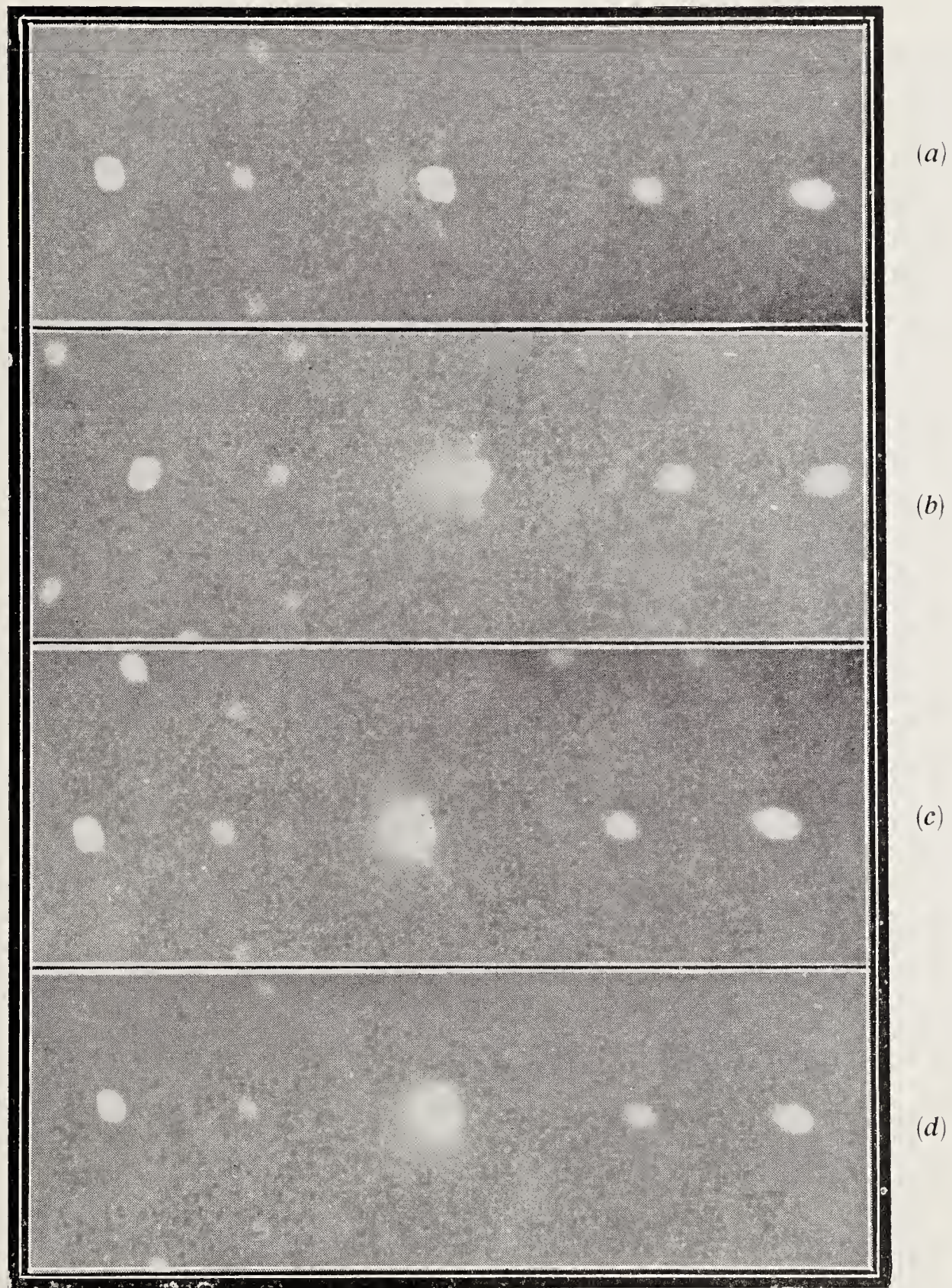


FIG. 1. Exhibiting the dynamic reflections by the (220) planes at various settings.



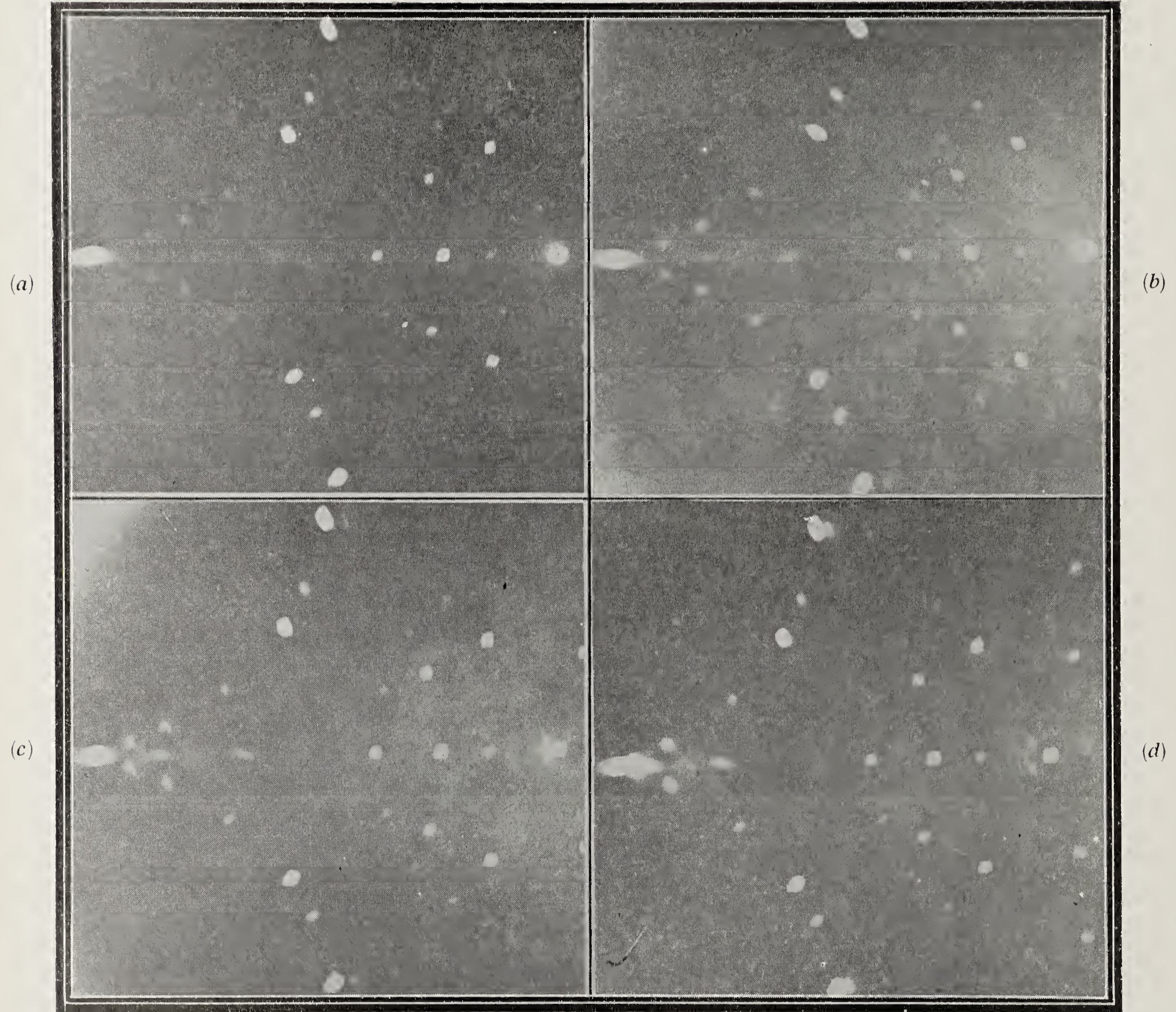


FIG. 1. Exhibiting the dynamic reflections by the (111) planes at the left and by the (113) planes at the right.



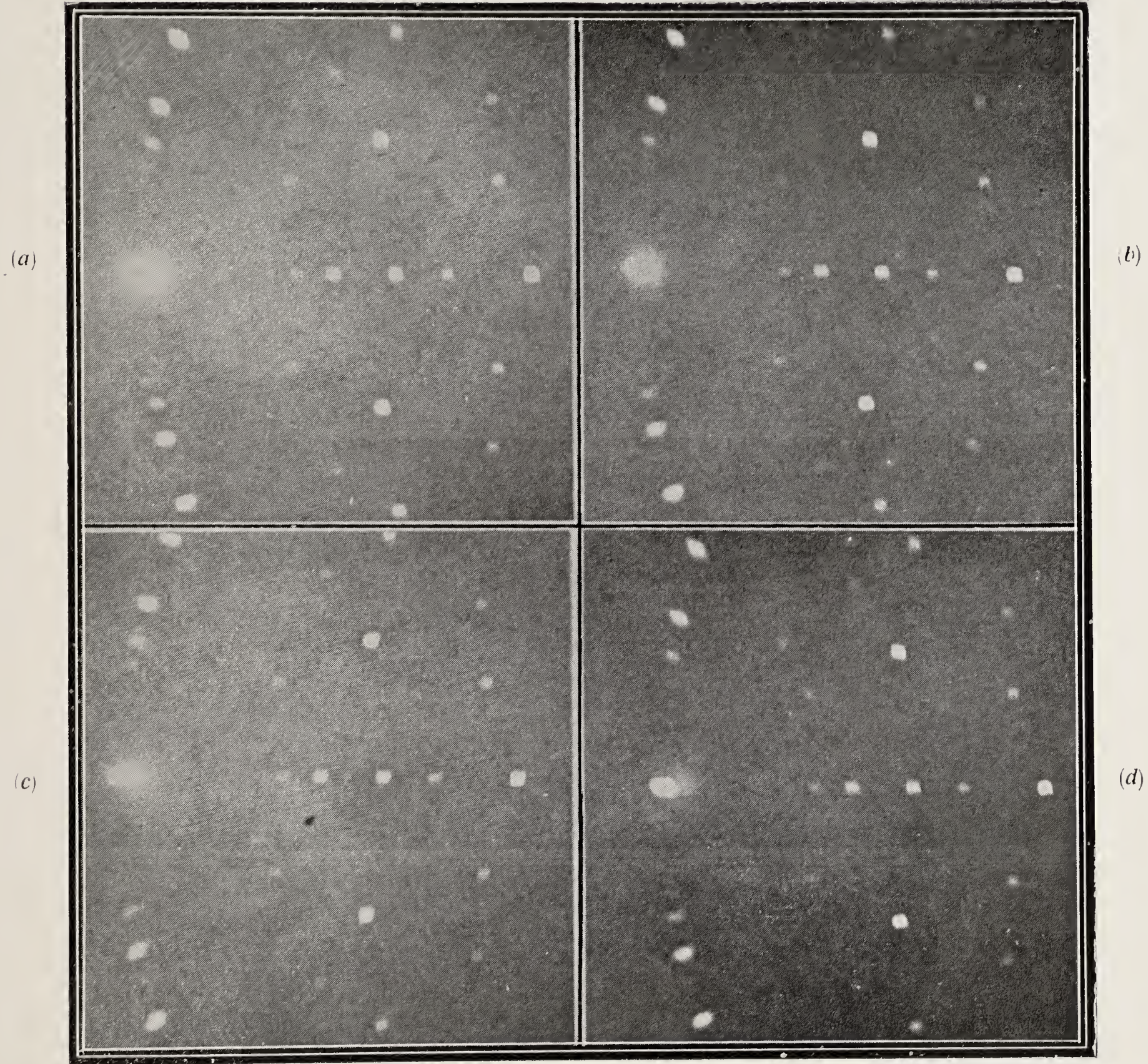


FIG. 1. Exhibiting the dynamic reflections by the (400) planes at the left.



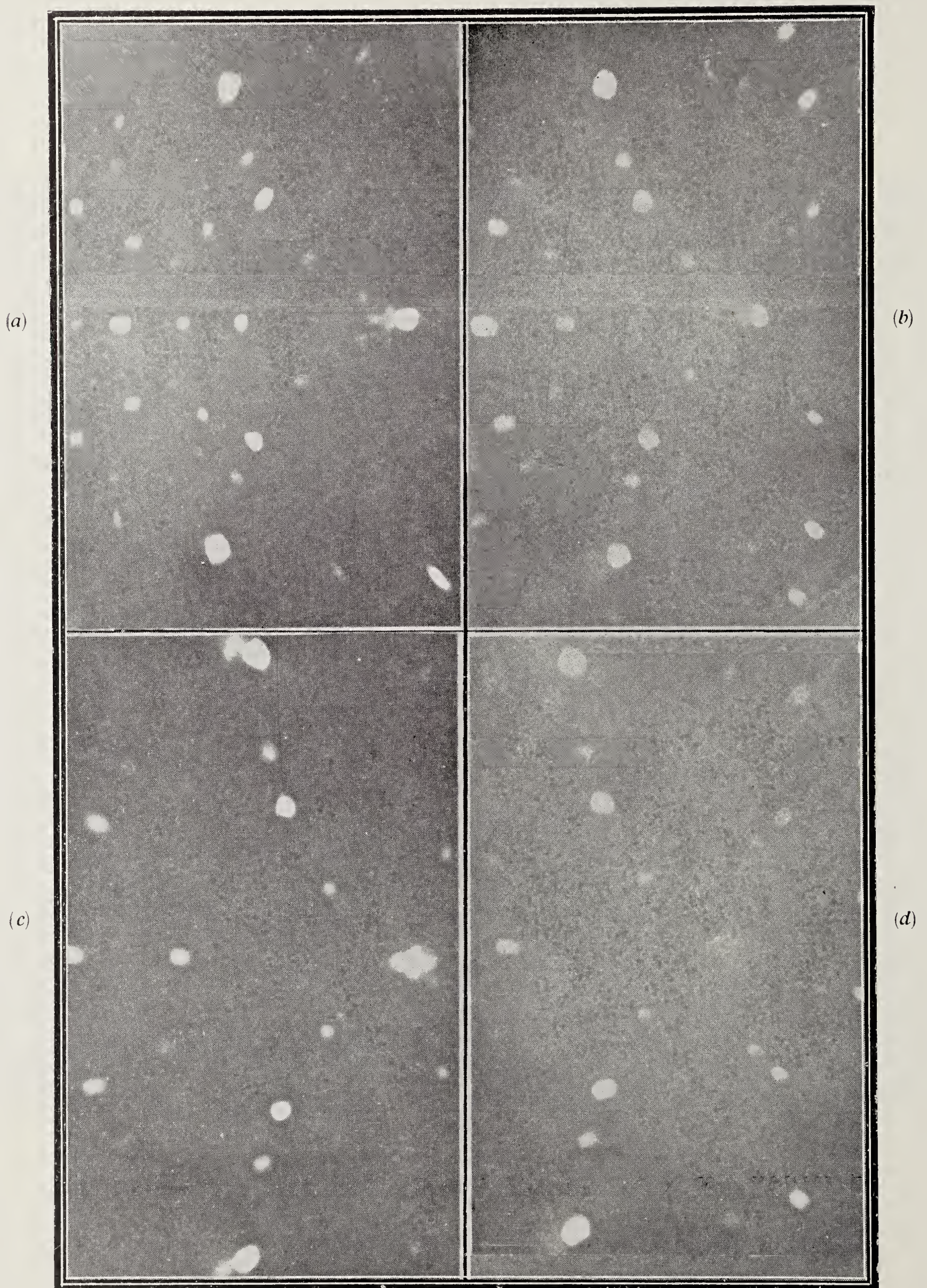


FIG. 1. Exhibiting the dynamic reflections by the (111) planes of tetrahedral diamond on the left and their absence with octahedral diamond on the right.



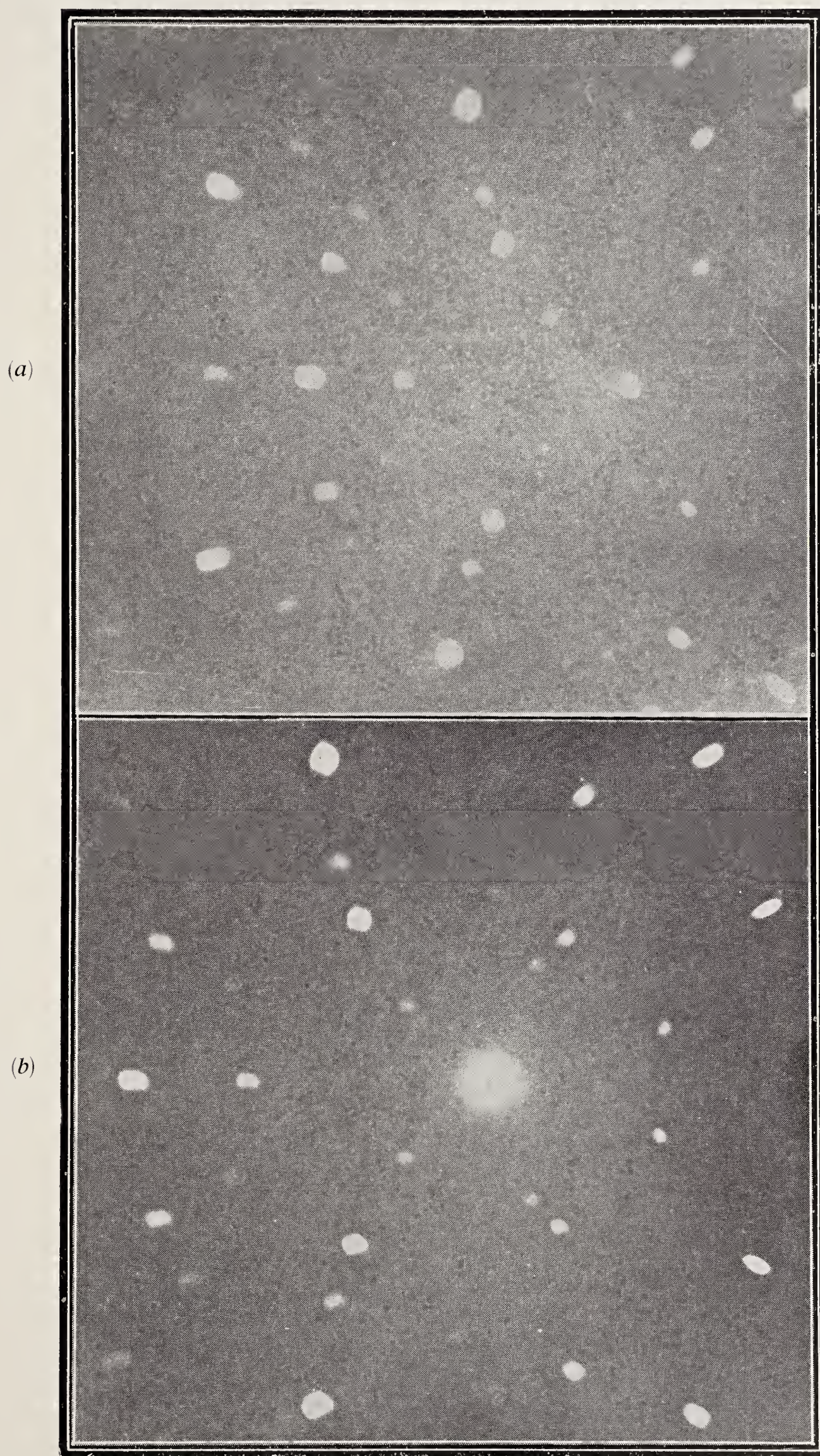


FIG. 1. Laue patterns of octahedral diamond showing intense reflection by the (111) planes at different settings.



(a)

(b)

(c)

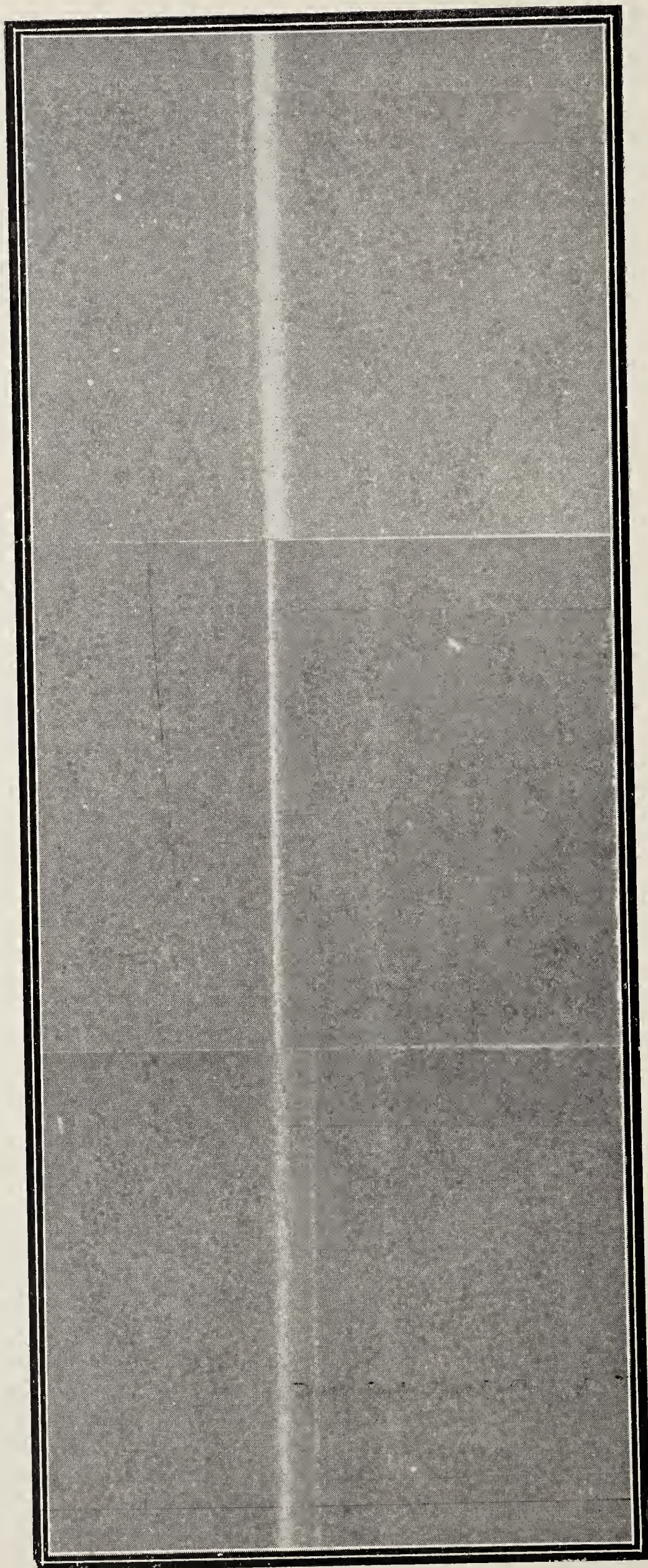


FIG. 1. For explanation, see text.



## THE HEAT CAPACITY OF DIAMOND BETWEEN 0 AND 1000° K.

BY SIR C. V. RAMAN

(Memoir No. 103 of the Raman Research Institute, Bangalore-6)

Received November 14, 1957

### 1. INTRODUCTION

THE evaluation of the heat capacity of diamond on the basis of the theory of specific heats of crystals advanced by the author formed the subject of a recent publication<sup>1</sup> in these *Proceedings*. Since then, fresh experimental determinations have been reported which go down to temperatures at which the value of  $C_p$  for diamond is as low as 0.0001, in other words only a fifty-thousandth part of its value 5.0 at 1000° K. which is itself smaller than the theoretical maximum of 5.96 for a monatomic solid. We proceed here to consider the new experimental results. The theoretical evaluation already published succeeds in explaining the change of  $C_p$  with temperature over the whole of this enormous range of values in a highly satisfactory manner, but with certain reservations made necessary by the fact that the theoretical calculations are based on the spectroscopic behaviour of ideal diamonds, whereas the reported determinations have been made with material which is very far indeed from being ideal. To exhibit the closeness of the agreement which is observed over practically the entire temperature range as well as the minor differences which are noticeable in certain limited parts of it, the data have been plotted on adequate scales alongside of the theoretical values in a series of graphs which are reproduced in the present paper. The cause of the small differences which appear in the temperature range between 50 and 150° K. is discussed and it is shown that they are explicable in terms of the differences in the spectroscopic behaviour of ideal and non-ideal diamonds.

Diamond illustrates in a most striking manner the fundamental relationship between the specific heats of crystals and their spectroscopic behaviour. Being an elementary solid crystallising in the cubic system with an exceptionally simple structure, the characteristic modes of atomic vibration which determine both the thermal behaviour and the spectroscopic properties of diamond can be described in geometric terms without any reference to the magnitude of the interatomic force constants. Considerations of a general nature enable us to go further and arrange these modes in a scale of descending frequency, thereby greatly facilitating their identification.



Diamond being a transparent solid, the modes and frequencies of atomic vibration in it are also accessible to observation by a variety of spectroscopic methods. It is found possible to determine these frequencies with precision and compare them with the theoretically computed values. Thus theory and experiment agree to give us a complete and detailed picture of the atomic vibration spectrum of diamond. It thereby becomes possible to evaluate the heat capacity of the crystal in a completely independent fashion involving no assumptions of any sort. The agreement which emerges between the results of such evaluation and the experimental data is a convincing demonstration of the correctness of the theoretical approach.

## 2. THE VIBRATION SPECTRUM OF DIAMOND

The crystal structure of diamond consists of two distinct sets of atoms of carbon which appear separately in layers parallel to the faces of the octahedron and the cube respectively. The normal modes of atomic vibration of the structure can be readily described in terms of this arrangement. The principal mode of vibration is an oscillation of the two sets of atoms with respect to each other along any one of the three cubic axes and has therefore a degeneracy of 3. The atoms present in the layers parallel to the octahedral faces may oscillate with respect to each other either normally or transversely to themselves with degeneracies of four and eight respectively; but since the adjacent non-equivalent layers may oscillate either in the same or opposite phases, we have two such sets of modes. Likewise, we have two sets of modes in which the layers of atoms parallel to the cube faces oscillate normally or transversely to themselves with degeneracies of three and six respectively. Thus, we have 9 distinct normal modes with degeneracies of 3, 4, 4, 8, 8, 3, 3, 6 and 6 respectively, making a total of 45 modes in all. Considering the set of 16 atoms contained in a volume element which is twice as large in each direction as the unit cell of the crystal structure, the total number of atomic degrees of freedom of this group is 48. The 45 modes of vibration described above may be regarded as the *modes of internal vibration of this group*, while the three degrees of freedom left over represent *its three translations*.

In a lecture on the diamond delivered at Zurich, Freiburg and Bonn in July 1956, and subsequently published in these *Proceedings*<sup>2</sup> it was shown in detail how the frequencies of the nine normal modes described above may be evaluated and checked against the frequency shifts observed in the scattering of light by diamond when it is traversed by the  $\lambda$  2536.5 radiations of the mercury arc. We shall content ourselves here with reproducing below as Fig. 1 a chart showing the nine frequencies and their respective degeneracies.



The two modes of oscillation normal to the cubic planes have an identical frequency of  $1088\text{ cm.}^{-1}$ . They have accordingly been shown as a single frequency with a degeneracy of 6.

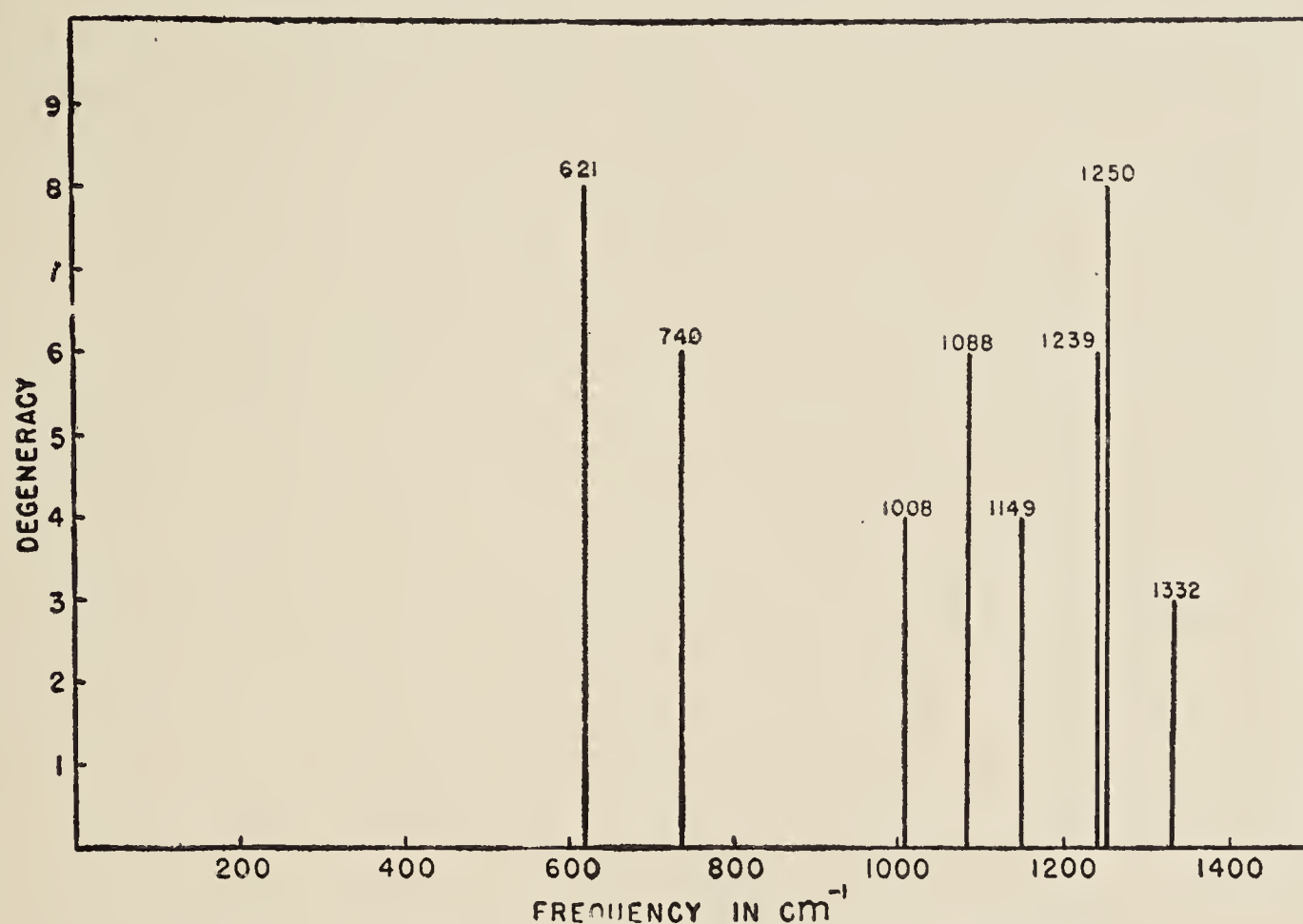


FIG. 1. Chart of the Vibration Spectrum of Diamond.

To complete the picture, we require to know how the three translatory movements of the 16-atom group manifest themselves in the vibration spectrum of the crystal. It is obvious that they would appear as internal vibrations in volume elements of larger size than the 16-atom group and therefore having lower frequencies. In dealing with vibrations of this nature, it is permissible to ignore the discrete atomic structure of the material. The larger the size of a volume element is, the lower would be the frequencies of its internal vibration. Considering volume elements of all possible sizes as the oscillators, their frequencies of internal vibration would evidently range from the lowest possible value  $\nu = 0$  to an upper limit  $\nu_L$  which may be taken equal to the lowest of the frequencies of vibration appearing in the chart (Fig. 1). The manner in which the disposable degrees of freedom of atomic movement are distributed over this range of frequencies is indicated by a simple argument. The number of volume elements of any specified dimension included in the crystal and hence also the number of degrees of freedom represented by their translations diminish in inverse proportion to the cube of the linear dimensions, while the frequencies of their internal vibration would vary inversely as the first power of the same. Hence the number of degrees of freedom appearing as internal vibrations of the volume



elements and having frequencies between 0 and  $\nu$  would be proportional to  $\nu^3$ . By differentiation, we obtain the result that the number of degrees of freedom appearing between frequencies  $\nu$  and  $\nu + d\nu$ , in other words, the number of oscillators in the crystal having frequencies in that range would be proportional to  $3\nu^2 d\nu$ . The constant of proportionality may be deduced at once from the consideration that on integration between zero and the upper limit  $\nu_L$ , we should obtain as the total number of oscillators three times the number of 16-atom groups comprised in the crystal.

### 3. THE HEAT CAPACITY OF DIAMOND

Having thus ascertained the nature of the complete vibration spectrum of diamond, we proceed to make use of the theory of Einstein and obtain an expression for the heat content of the crystal as a function of the temperature. This appears as a sum of two quantities; the first is a summation of the average energies of the individual oscillators having the discrete frequencies shown in the chart (Fig. 1) multiplied by their respective degeneracies and by the total number of 16-atom groups contained in the crystal. The second part is a summation of the average energies of vibration of the oscillators of larger sizes having various frequencies from 0 to  $\nu_L$ , and this takes the form of an integral between these limits of frequency. The details of the calculations have already been given in the earlier paper and it is therefore sufficient to reproduce here the final results here in tabular form.

TABLE I  
*Theoretical Computation of the Atomic Heat of Diamond*  
(Calories per gram-atom per degree)

Absolute Temperature	Discrete Frequencies	Residual Spectrum	Total	Absolute Temperature	Discrete Frequencies	Residual Spectrum	Total
15°	..	0.00014	0.00014	200	0.4069	0.1631	0.5700
20	..	0.00033	0.00033	225	0.5894	0.1895	0.7789
25	..	0.00064	0.00064	250	0.7844	0.2124	0.9968
30	..	0.0011	0.0011	275	1.0137	0.2319	1.2456
40	..	0.0026	0.0026	300	1.2418	0.2486	1.4904
50	..	0.0051	0.0051	350	1.700	0.275	1.975
60	..	0.0088	0.0088	400	2.139	0.294	2.433
70	0.0005	0.0140	0.0145	450	2.538	0.308	2.846
80	0.002	0.0207	0.0227	500	2.892	0.319	3.211
90	0.0056	0.0290	0.0346	600	3.469	0.334	3.803
100	0.0128	0.0388	0.0516	700	3.899	0.344	4.243
120	0.0419	0.0619	0.1038	800	4.24	0.350	4.574
140	0.0957	0.0877	0.1834	900	4.465	0.355	4.820
160	0.1758	0.114	0.2898	1000	4.653	0.358	5.011
175	0.2517	0.1333	0.3850	1100	4.797	0.360	5.157



It will be seen that the contribution from the set of discrete frequencies becomes negligible at temperatures below 60° Abs. At and below that temperature, the residual spectrum of frequencies alone is responsible for the entire heat capacity of the crystal. At higher temperatures, however, the contribution of the spectrum of discrete frequencies rapidly increases and ultimately becomes responsible for all except 1/16th part of the specific heat.

In order to exhibit the over-all success of the theory in explaining the thermal behaviour of diamond, the figures for the atomic heat shown in Table I have been plotted as a curve (Fig. 2) on a scale which is adequate

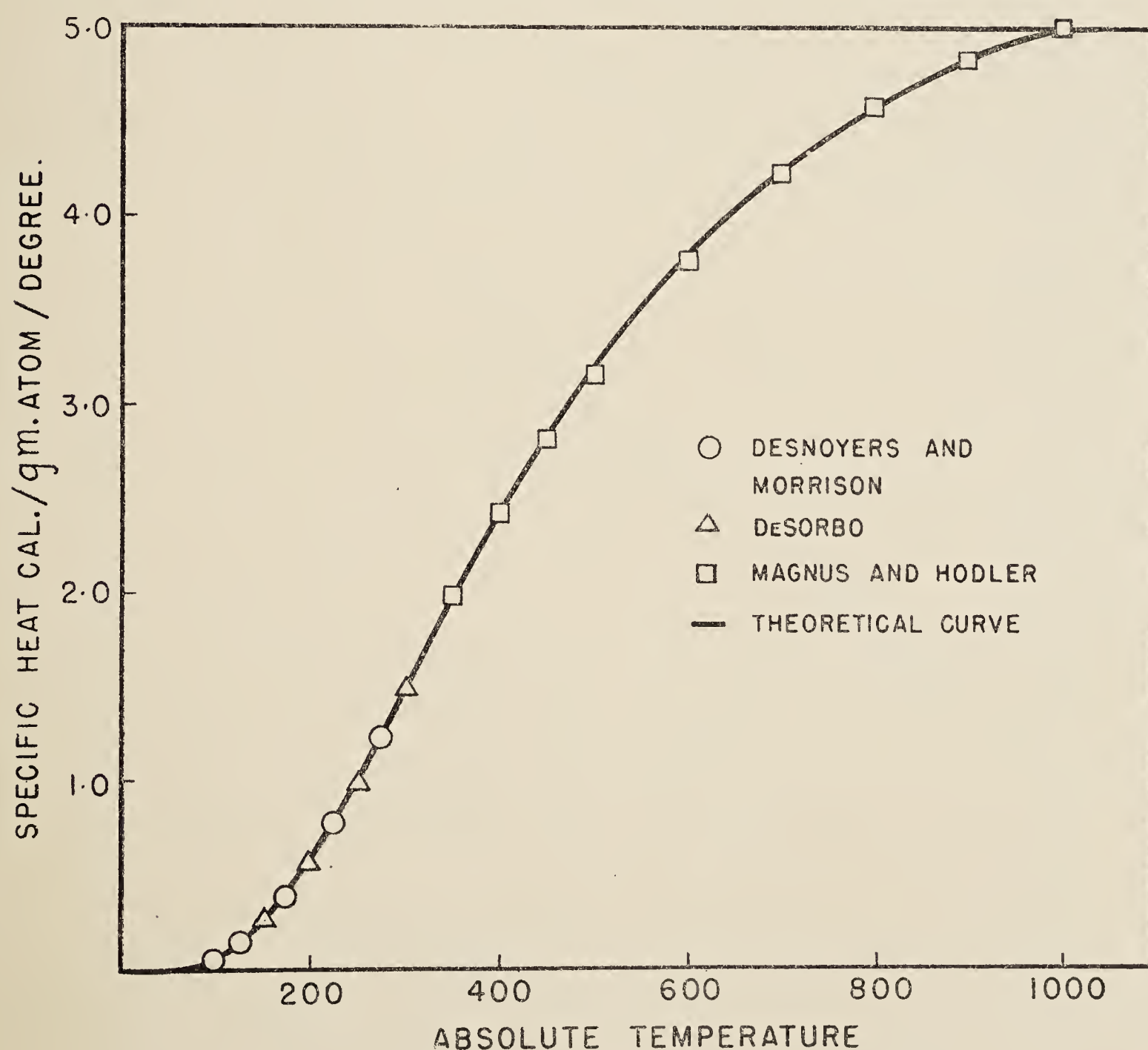


FIG. 2. Specific Heat of Diamond from 0 to 1000°.

to represent the data except in the region where it runs nearly parallel to the axis of temperature. In the temperature range between 300 and 1000° K., the values determined by Magnus and Hodler have been used, while in the



lower ranges, the data of DeSorbo as well as those reported by Desnoyers and Morrison have been put in. It will be seen that no deviations between theory and experiment which are at all significant are noticeable on the scale of the graph.

For temperatures below  $300^{\circ}$ , the determinations by Pitzer, DeSorbo and by Desnoyers and Morrison are available, but since the two latter sets of determinations are in good agreement, they have been plotted in a graph covering the temperature range between 160 and  $300^{\circ}$  K. (Fig. 3). The

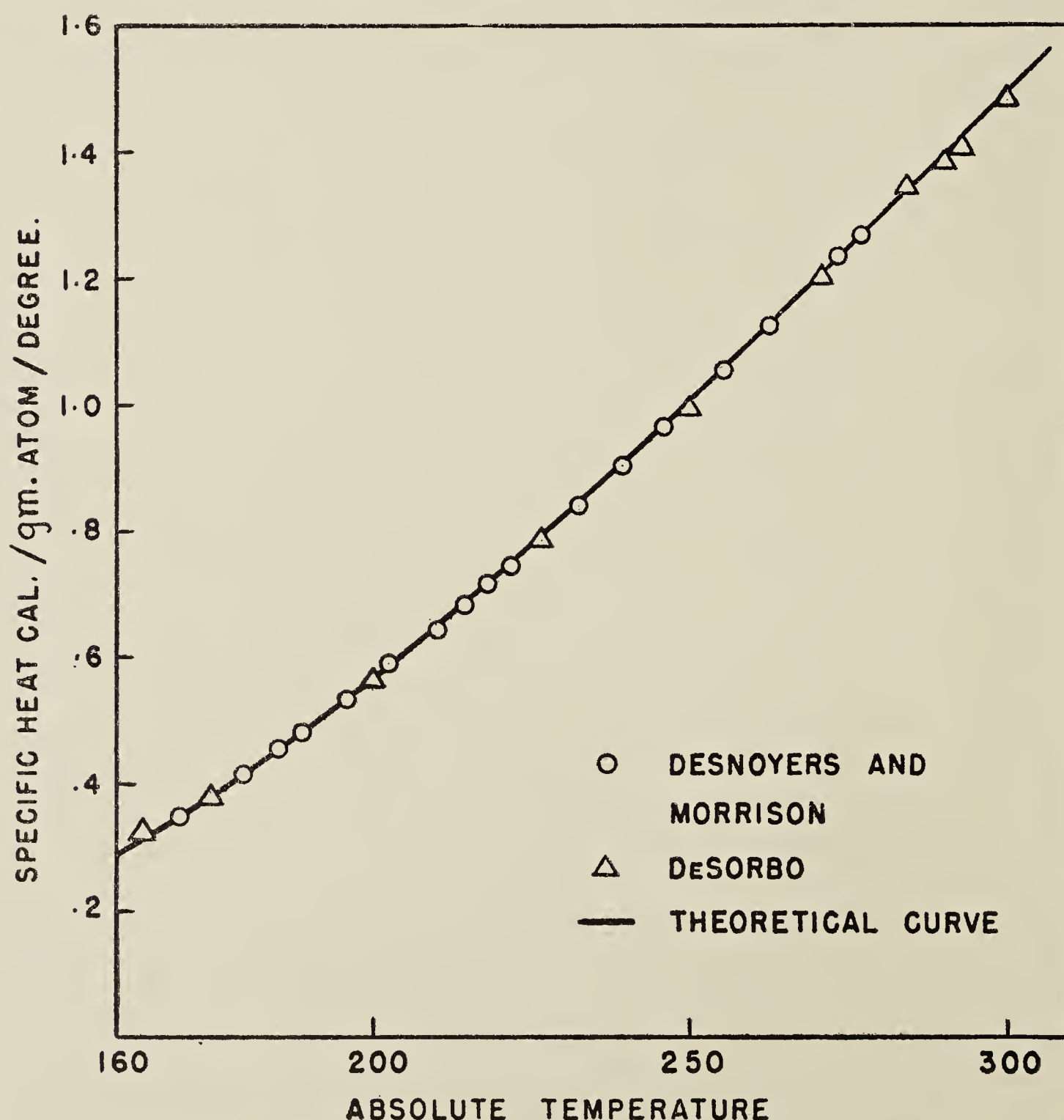


FIG. 3. Specific Heat of Diamond from 160 to  $300^{\circ}$ .

scale on which this figure has been drawn is adequate to disclose any systematic deviations between theory and experiment, had such existed. No such deviations are noticeable and hence it is evident that throughout the range of temperature in which the spectrum of discrete frequencies is principally



responsible for the heat capacity of diamond (160 to 1000° K.), the theory is in very satisfactory accord with the facts.

We shall next consider the very lowest temperatures where the value of  $C_p$  retreats into the third or fourth decimal place. The theoretical curve for this region has been drawn in Fig. 4, an adequately large scale being used for the ordinates, and the data reported by DeSorbo and by Desnoyers and Morrison have been plotted alongside of it. At the lowest temperatures the values of DeSorbo exhibit a distinct scatter, many of them lying above the theoretical curve. On the other hand, the more recent data of Desnoyers and Morrison lie smoothly on the curve up to 50°. The agreement between theory and experiment in this range made apparent by the graph must be considered highly satisfactory.

In the temperature range between 50° and 60° K., the experimental values plotted in Fig. 4 lie above the theoretical curve, the magnitude of the differences being a few units in the fourth place of decimals. From Fig. 5 which

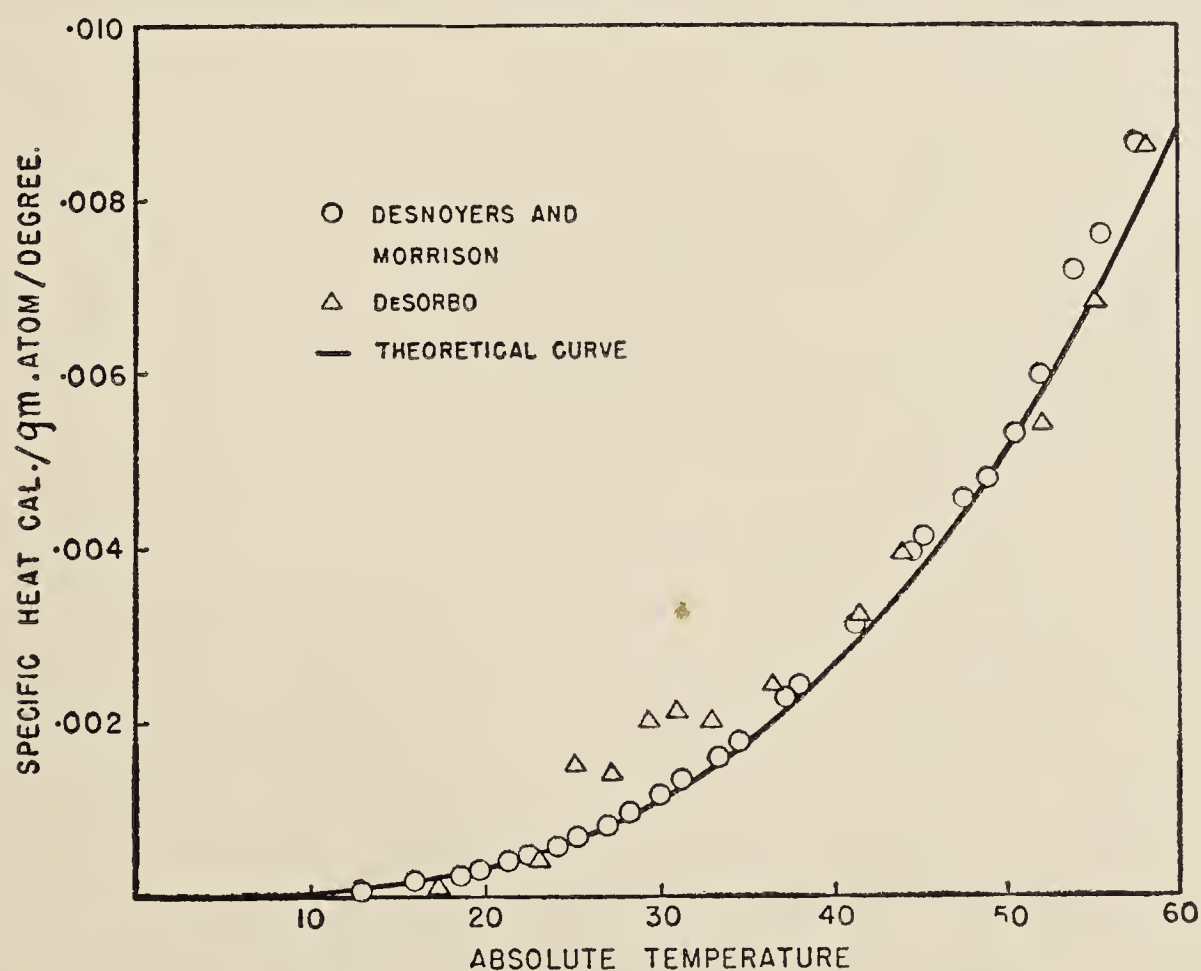


FIG. 4. Specific Heat of Diamond from 0 to 60°.

represents a comparison between theory and experiment in the range between 60 and 160° K. it will be seen that such differences become distinctly more pronounced at higher temperatures, reaching a maximum value of 0.007 at about 100°; they steadily diminish again at higher temperatures and finally cease to be noticeable on the graphs beyond 150° K. Since the value of the specific heat at 100° K. is itself very low, being only 0.059, the difference



between theory and experiment expressed as a percentage of the specific heat is 12%, but to express the difference in this way exaggerates its significance. Since, however, the discrepancy is real, we shall consider and comment upon its origin.

#### 4. SPECTROSCOPIC BEHAVIOUR OF NON-IDEAL DIAMONDS

An explanation of the differences which are noticeable between theory and observation in the values of  $C_p$  in the range between 50 and 150° K. is not far to seek. The theoretical calculations refer to the case of an ideal crystal. They could therefore be expected to show a complete agreement with the experimentally determined specific heats if only the latter had also been made with ideal diamonds. Actually, however, determinations of specific heat require fairly large masses of material and it is therefore inevitable that they are made with diamonds of an inferior sort. It may be noted that DeSorbo used 80 grams of fragmented bort. He noticed that some of the crystals exhibited colour and also that about 20% of the material was fluorescent. Desnoyers and Morrison report that the sample used by them consisted approximately of 160 grams of industrial diamonds, their average dimensions being about 3 mm. They also remark that most of their diamonds were lightly coloured, either yellow, brown or green but that none contained occlusions. It is evident from these descriptions that we are concerned here with the class of diamond that exhibits its non-ideality of crystal structure in a visible manner, in other words, shows colour in daylight and luminescence under ultra-violet illumination.

The spectroscopic behaviour of diamonds of all sorts has been investigated by a variety of methods over a period of many years by the author and his collaborators. It will suffice here to refer to the results reported in a paper by Miss Anna Mani<sup>3</sup> recording a detailed study of the fluorescence and absorption spectra of twenty-two diamonds of various sorts. When the crystals are cooled down to liquid air temperature, these spectra sharpen notably, and it then becomes possible to analyse them in detail. Inter-comparison of the fluorescence and absorption spectra enables the frequencies representing electronic transitions to be identified and distinguished from those due to the vibrational transitions appearing in combination with them. The result emerges clearly that the spectroscopic behaviour of diamonds which are colourless as seen by daylight and of those which exhibit various shades of brown, yellow or green is strikingly different. Diamonds of the former sort exhibit a blue fluorescence and the atomic vibration spectrum deduced from studies thereof is generally similar to that shown in the chart



reproduced above as Fig. 1 in the text. On the other hand, diamonds exhibiting visible tints by daylight fluoresce with a greenish yellow colour, the analysis of the spectrum of which discloses many features both in the electronic and atomic vibration spectra which are absent in the blue luminescence of

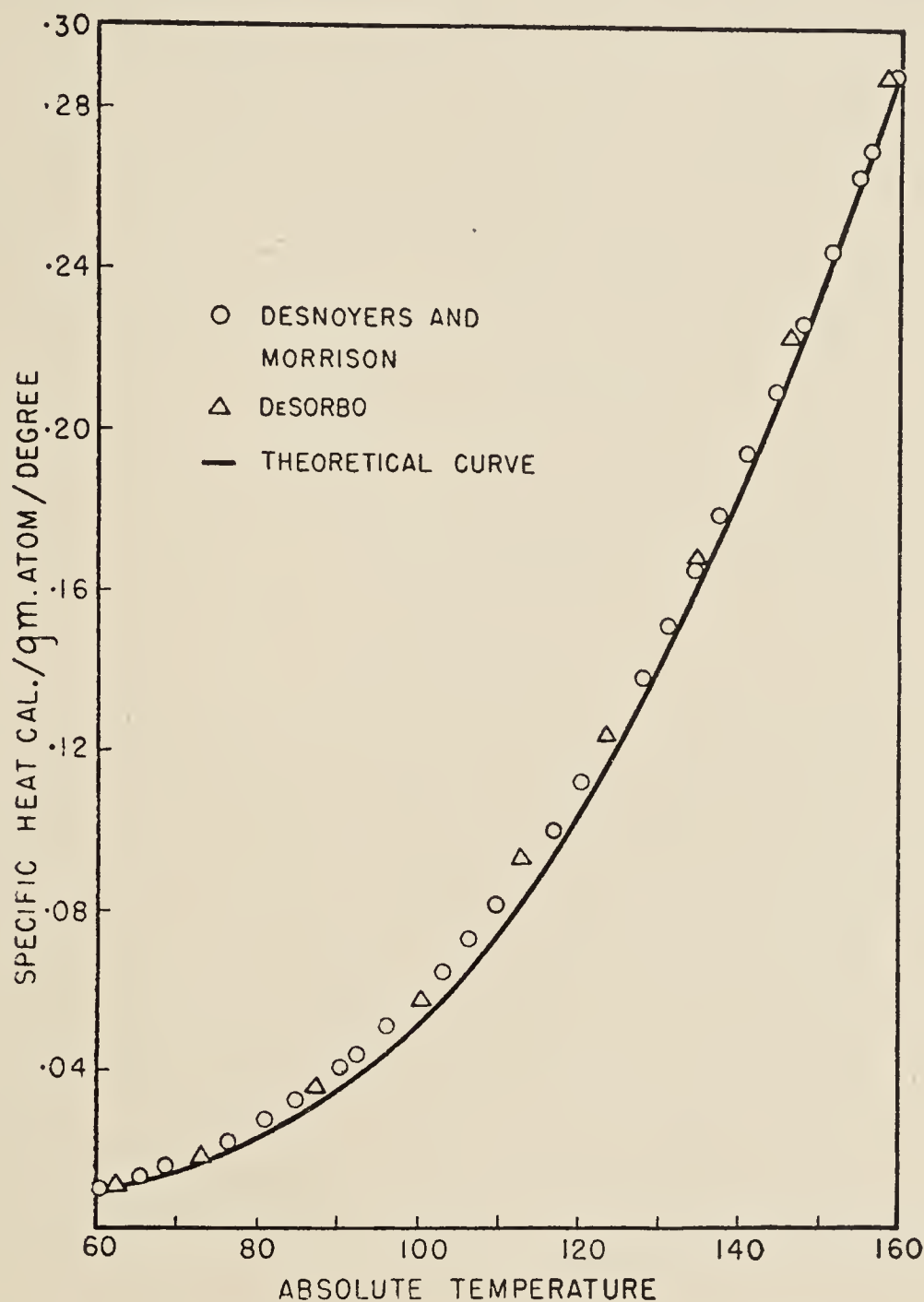


FIG. 5. Specific Heat of Diamond from 60 to 160°.

colourless diamonds. The most prominent of the additional features in the vibration spectrum is a band stretching from 257 to 443  $\text{cm}^{-1}$  with its peak at 359  $\text{cm}^{-1}$

It is clear from the facts recited above that the atomic vibration spectrum of non-ideal diamonds differs notably from that of the ideal material. The difference arises chiefly in the region of the residual spectrum of frequencies and may be described as an enhancement of its strength in the region of frequencies about 359  $\text{cm}^{-1}$ . Since the total number of atomic degrees of freedom is invariant, such enhancement would necessarily involve a diminu-



tion in the strength of the residual spectrum at higher frequencies between  $359\text{ cm.}^{-1}$  and the upper limit of  $621\text{ cm.}^{-1}$ . A change in the character of the residual spectrum of the nature indicated would evidently result in altering the specific heat of the crystal. The Einstein function for a frequency of  $359\text{ cm.}^{-1}$  has a negligible value at temperatures below  $50^\circ\text{ K.}$  It increases most rapidly in the temperature range in the vicinity of  $100^\circ$ , and at higher temperatures tends more slowly towards its limiting value. The change in the character of the residual spectrum would thus result in an increase of the specific heat of non-ideal diamonds which would be vanishingly small at very low and at very high temperatures and would be most prominent at about  $100^\circ\text{ K.}$  This describes what is actually observed.

#### ACKNOWLEDGEMENT

The author much appreciates the courtesy of Messrs. Desnoyers and Morrison in having made the results of their valuable new determinations available to him in advance of publication.

#### SUMMARY

The evaluation of the heat capacity of diamond on the basis of the theory of specific heats advanced by the author is discussed and the results are compared graphically with the latest available experimental data. A striking over-all agreement emerges over the whole of the temperature range between  $0$  to  $1000^\circ\text{ K.}$  The experimental values are however slightly in excess of the theoretical ones in the limited range between  $50$  and  $150^\circ\text{ K.}$ , the difference in the value of  $C_p$  being a maximum of  $0.007$  at about  $100^\circ\text{ K.}$  and ceasing to be noticeable both below  $50^\circ\text{ K.}$  and above  $150^\circ\text{ K.}$  This small excess is explained as a consequence of the use in the experimental determinations of industrial diamonds whose spectroscopic behaviour is observably different from that of the ideal material.

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- |              |  |
|--------------|--|
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| Anna Mani    | .. <i>Ibid.</i> , 1944, <b>19</b> , 231.                 |



## THE TETRAHEDRAL CARBON ATOM AND THE STRUCTURE OF DIAMOND\*

BY SIR C. V. RAMAN

(Memoir No. 104 from the Raman Research Institute, Bangalore 6)

### 1. INTRODUCTION

MY address to the Academy this year concerns itself with the element carbon and its chemical behaviour. The importance of this subject hardly needs to be stressed. Indeed, the amazing power which the atoms of carbon display of combining with themselves and with other atoms to form an immense variety of distinct compounds is one of the marvels of nature. It is perhaps part of the secret of life itself.

The science of chemistry made a great step forwards when it was realised that the structure of a chemical molecule can only be properly described in terms of the configuration in three-dimensional space of the atoms of which it is composed. This approach to chemical problems made its debut in the year 1874 when Van't Hoff put forward his famous hypothesis of the tetrahedral carbon atom. What that description of the carbon atom really signifies, the physical and chemical evidence on which our belief in its validity is based and the explanation of the chemical behaviour of carbon in terms of the ultimate structure of its atoms are the topics which we shall proceed to consider. The ideas which emerge from the discussion will then be applied to an elucidation of the crystal structure of diamond and the explanation of the properties of that remarkable substance.

### 2. THE FOUR VALENCES OF CARBON

The simplest molecules exhibiting the disposition in space of the valences of the carbon atom are those in which an atom of carbon combines with four similar atoms or similar groups of atoms. This situation exists, for example, in the cases of methane ( $\text{CH}_4$ ), deuteromethane ( $\text{CD}_4$ ), carbon tetrafluoride ( $\text{CF}_4$ ), carbon tetrachloride ( $\text{CCl}_4$ ), carbon tetrabromide ( $\text{CBr}_4$ ), tetramethyl methane  $[\text{C}(\text{CH}_3)_4]$  and so forth. In all these cases, the atoms or atomic groups which combine with the carbon atom are found to be disposed in space with perfect tetrahedral symmetry round it. This is most convincingly shown by the study of the vibration spectra of these molecules.

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\* Presidential Address to the Indian Academy of Sciences at the Tirupati Meeting on the 28th December, 1957.



A molecule composed of five atoms would in general exhibit nine modes of free vibration. On the other hand, the five-atom groups listed above exhibit only four fundamental frequencies of vibration. Such a reduction would follow as a necessary consequence of the molecule possessing perfect tetrahedral symmetry. It is therefore to be regarded as demonstrating that the atoms in these molecules are located at the vertices of a regular tetrahedron with the carbon atom itself at its centre.

The vibration spectra of molecules in which an atom of carbon combines with three atoms of one kind and a fourth of a different kind show that in every such case, they have six fundamental vibration frequencies and no more. As examples of this behaviour may be listed the molecules of  $\text{DCH}_3$ ,  $\text{HCD}_3$ ,  $\text{HCF}_3$ ,  $\text{FCH}_3$ ,  $\text{HCCl}_3$ ,  $\text{DCCl}_3$ ,  $\text{FCCl}_3$ ,  $\text{ClCH}_3$ ,  $\text{ClCD}_3$ ,  $\text{BrCH}_3$ ,  $\text{BrCD}_3$  and  $\text{ICH}_3$ . Dynamical theory shows that a five-atom group possessing a triad axis of symmetry would exhibit only six distinct frequencies instead of nine. The observed facts are thus a clear proof that the molecules listed do possess such a symmetry. On the other hand, molecules containing carbon combining with two atoms of one kind and two atoms of another kind should exhibit all the nine modes of vibration, and this is in agreement with experience.

The symmetry of form of the molecules in each of the cases referred to above can also be inferred from the numbers respectively of polarised and depolarised lines observed as frequency shifts in the spectra of light-scattering. Here again, the experimental facts confirm the tetrahedral character of the atomic grouping around the central carbon atom.

Studies on the vibration spectra of various molecules of the kind quoted above also furnish us with a convincing proof of the non-existence of the several isomers which may be expected to be forthcoming if the four valences of carbon were not equivalent. For, the vibration frequencies of the molecules would be influenced by the atomic configurations and each isomer would therefore have its own set of vibration frequencies. As the characteristic frequencies reveal themselves as well-defined lines in the spectrum, multiplication of the number of observed frequencies would follow as a consequence of the existence of more than one form of the molecule. As no such effect is observed in the numerous cases which have been studied, we are justified in inferring that such isomers do not exist.

A question of great importance which arises in regard to molecules in which an atom of carbon is joined to four others which are not all the same is whether their joins with it make equal angles with each other as is



to be expected if the valences were directed along the axes of a regular tetrahedron. This question can only be answered if methods for precise determination of the atomic configurations were available. Two such methods have been employed for the determination of the atomic configurations in molecules, namely, X-ray diffraction and electron diffraction. Both of these methods involve recondite theoretical considerations besides complicated calculations. The results derived from them must therefore be considered as subject to some measure of uncertainty and this has to be borne in mind in assessing the significance of the reported results. Pauling, in his book '*On the Nature of the Chemical Bond*' (Second Edition, 1940, Table 14-I) gives a list of sixteen carbon compounds of varying degrees of complexity whose molecular structure has been investigated by electron diffraction methods. The table of results gives the bond angle subtended at the carbon atom for eight different species of bonds, namely, C-C-C, C-C-Cl, C-C-Br, F-C-F, Cl-C-Cl, Br-C-Br, F-C-Cl and N-C-N. In five of these cases, namely, C-C-Br, C-C-Cl, F-C-F, F-C-Cl and N-C-N the angles are indistinguishable from the tetrahedral angle of  $109^{\circ} 28'$ , while in the three other cases, namely, Cl-C-Cl, C-C-C and Br-C-Br the reported bond angles exceed the tetrahedral angles by a degree or two; but this difference cannot be regarded as significant since the reported experimental uncertainties are of the same order of magnitude.

We may sum up the conclusions which may be legitimately drawn from the facts of experiment cited above as follows: *When an atom of carbon combines with four others, the four valences are directed along the four axes of a regular tetrahedron but are otherwise indistinguishable from each other.*

### 3. THE ATOMIC STRUCTURE OF CARBON

The interpretation which has to be placed on the results stated above becomes clear when we take note of the position of carbon in a list of the chemical elements arranged in the order of atomic numbers, that is to say, according to the magnitude of charge on the nucleus of the atom or the number of the electrons outside the nucleus. In such a list, the chemically inert gas helium occupies the second position, and the chemically inert neon occupies the tenth, while carbon with its six electrons occupies a position midway between them. Likewise, silicon which in several respects exhibits a chemical behaviour similar to carbon and has fourteen electrons stands midway between the inert gases neon and argon which have respectively ten and eighteen electrons outside their atomic nuclei. This is an example of the periodicity in chemical behaviour which makes itself evident when the elements are listed in the order of their atomic numbers. Such periodicity



finds its explanation in certain general features manifested in the building up of the atoms, viz., the arrangement of the extra-nuclear electrons in a series of shells denoted respectively as K, L, M, etc. When the K shell is complete with its two electrons, we have the inert gas helium; when the L shell is also complete with its eight additional electrons, we have the inert gas neon; when a further eight electrons have been put into the M shell, we have the inert gas argon. Thus it is clear that the quadrivalence of carbon arises from the fact that it has four electrons in the L shell, just half the full quota of eight electrons needed to complete that shell. Further, since the valences are directed along the four axes of a regular tetrahedron, we are evidently concerned here with a state of the atom in which the four electrons in the L shell by reason of their interactions with each other and with the force field of the charged core of the atom constitute a system which is electrically neutral but exhibits perfect tetrahedral symmetry. This system may therefore be rightly designated as the tetrahedral carbon atom. It can combine with four other atoms or groups of atoms to form molecules, but does not depart sensibly from its tetrahedral symmetry of structure as the result of such combination.

We have now to ask ourselves what precisely are the circumstances which favour the formation of the tetrahedral quartet of electrons referred to above. It is well known that helium, neon and argon besides being chemically inert are also diamagnetic in their behaviour. The explanation given for the latter circumstance is that in the building up of the electronic clouds, the magnetic moments arising from the inherent spins of the electrons as well as those, if any, arising from their orbital movements around the nucleus mutually cancel each other out. The same circumstance is also responsible for the chemical inertness of these gases. For this to happen in the L shell of an atom we require eight electrons, but since there are only four present in the L shell of carbon, the same situation cannot arise in its case. But the question does arise as to how the angular momenta associated with the orbital motion and the inherent spins of the four electrons are disposed. If the configuration resulting from the mutual interactions of the four electrons is to possess full tetrahedral symmetry, it is clearly necessary that the resultant angular momenta associated with each of the four electrons considered individually should be equal and that further, these momenta should set themselves respectively along the four axes of a regular tetrahedron. The total angular momentum of the quartet and hence also its magnetic moment would vanish in these circumstances, and hence *the quartet of electrons must be considered as diamagnetic. But it would not*



*be chemically inert since the cancellation is a result of the tetrahedral setting of the individual angular momenta and not of their internal pairing off.*

An interesting consequence of the foregoing ideas should be here referred to. The angular momentum of an electron and hence also the magnetic moment associated with it is a vector and hence must be regarded as having both a direction and a sign. As already remarked, the directions in the present case are along the four axes of a regular tetrahedron, and if the quartet is to possess tetrahedral symmetry, all the four vectors concerned should have the same sense. Hence, they should all be directed either outwards or inwards from the core of the atom. Thus we have two distinct possible states of the tetrahedral carbon atom which we might designate as the  $\alpha$  and the  $\beta$  states respectively. These do not differ from each other except in the sense of the angular momenta of the individual electrons, these being directed respectively outwards or inwards from the charged core of the atom in the two cases.

#### 4. THE CRYSTAL STRUCTURE OF DIAMOND

Diamond furnishes a perfect illustration of Van'T Hoff's hypothesis of the tetrahedral carbon atom. For, X-ray analysis discloses its structure to consist of two sets of carbon atoms, each carbon atom in one set being chemically linked with perfect tetrahedral symmetry to four carbon atoms belonging to the other set and *vice versa*. The joins of the carbon atom in each set with the four others in the second set are all parallel to each other and to the four body-diagonals of a cube. Hence diamond exhibits the symmetry belonging to a crystal of the cubic class. Considering this situation in the light of the remarks made in the preceding section, it follows that diamond is a crystal whose properties would not be uniquely decided by the crystal structure alone as determined by the methods of X-ray analysis. Diamond consists of two interpenetrating lattices of carbon atoms. In an ideal crystal all the atoms belonging to one lattice should be the same, but as there are two possible types of tetrahedral carbon atom, it follows that an ideal diamond may belong to any one of four types, namely,  $\alpha\alpha$ ,  $\alpha\beta$ ,  $\beta\alpha$ , and  $\beta\beta$ . There is no reason to expect that these four types of diamond would exhibit any significant differences in such properties as lattice spacings, or the energy of formation, or the atomic vibration frequencies and so forth. But we should expect observable differences of a less obvious kind arising from the fact that the  $\alpha\alpha$  and  $\beta\beta$  types of diamond would possess a perfect octahedral symmetry in their crystal structure, whereas the two other types  $\alpha\beta$  and  $\beta\alpha$  would exhibit only the lower or tetrahedral symmetry.



Thus our present approach to the basic problems of organic chemistry leads to a natural and intelligible explanation of the fact that some diamonds exhibit infra-red absorption in the region of wave-lengths about  $8\ \mu$  including the characteristic lattice frequencies of vibration, while other diamonds do not exhibit this absorption. The diamonds which exhibit such absorption are those whose structure is of the  $\alpha\beta$  or  $\beta\alpha$  type, while those that do not are those whose structure is of the  $\alpha\alpha$  or  $\beta\beta$  type. Considerations of the same nature would also account for the differences exhibited by diamond in respect of other properties including especially the presence or absence of absorption of light in the near ultra-violet, which as is well known accompany the presence or absence of infra-red absorption in the  $8\ \mu$  region. We shall not enter into these questions here in detail but shall content ourselves with making two further remarks. The difference between the diamonds exhibiting octahedral and tetrahedral symmetry respectively cannot be expected to manifest itself in any difference in piezo-electric behaviour. The other remark is to recall the fact long known to mineralogists that the external forms of the diamond crystals found in nature more often than not indicate the lower or tetrahedral symmetry instead of the higher or octahedral one. This fact ceases to be surprising in the light of the considerations set forth above.

## 5. THE THEORY OF HYBRID BOND ORBITALS

We cannot avoid making some reference here to the attempts that have been made to explain the directed valences of the carbon atom in terms of ideas based on the Schrodinger solution of the wave-equation for the hydrogen atom. The theory of hybrid bond orbitals, as it is called, can be summarised as follows: The solution of the hydrogen problem by the Schrodinger method yields a series of solutions ( $s$ ,  $p$ ,  $d$ , etc.) which indicate the possible distributions of electron density around the nucleus. The wave-function  $s$  indicates a distribution of electron density spherically symmetrical round the nucleus, where there are three wave-functions denoted by  $p_x$ ,  $p_y$  and  $p_z$  respectively which represent density distributions whose maximum extensions are respectively along the  $x$ ,  $y$  and  $z$  axes in both directions. All these wave-functions represent the same energy and hence it is possible to construct linear combinations of them so as to produce new wave-functions which are orthogonal to each other. By giving equal weights to the wave-functions  $p_x$ ,  $p_y$  and  $p_z$  but different signs in different cases and adding the  $s$  wave-function, it is possible to obtain four wave-functions which are tetrahedrally symmetric with respect to the nucleus.



The four orbitals thus derived are put forward as a representation of the directed valences of a carbon atom.

Several criticisms of a fundamental nature regarding the theory thus briefly summarised may be put forward. The first objection is that we are not concerned here with a hydrogen atom having a single electron but with a carbon atom having two inner and four outer electrons; the interactions of these with each other and with the atomic nucleus are of the very essence of the problem but they are left out of consideration in the theory. A second objection is that the theory does not explicitly consider the spin of the electrons, though they play a fundamental role in the theory of atomic structure. Apart from these difficulties, one is also confronted with the fact that we have an infinite number of possible  $sp^3$  hybrids and the question may well be asked why the particular set which gives four orbitals indicative of a tetrahedral orientation of the valences should be chosen out of them all. The fundamental feature of the quadrivalence of carbon is that the tetrahedral disposition of the valences is maintained even when the four atoms with which the combination occurs differ from each other enormously, as for example, hydrogen, carbon, nitrogen, fluorine, bromine, chlorine and iodine—to mention no others. *It is this circumstance which indicates that the determining factor which gives rise to the tetrahedral configuration of the valences is not the energy of formation of the bond or bonds, but is an inherent property of the carbon atom itself.* In other words, it is to be found in the mutual interactions between the quartet of electrons which compel them to set themselves in a uniquely determined tetrahedral configuration.

## 6. SUMMARY

The experimental evidence derived from the study of the vibration spectra of molecules and of their electron diffraction patterns shows unequivocally that the four valences directed outwards from a carbon atom are parallel to the four axes of a regular tetrahedron. That this disposition is maintained even when the four atoms combining with the carbon atom differ enormously from each other indicates that we are concerned here with an intrinsic property of the carbon atom, namely, that the quartet of electrons in the L shell as a result of their mutual interactions can set themselves so as to constitute a structure possessing perfect tetrahedral symmetry. Such a structure would be diamagnetic but not chemically inert, since the individual angular momenta cancel out as a result of the tetrahedral setting and not as a consequence of the internal pairing off as in the inert gas molecules.



It follows from these considerations that there are two possible states of the carbon atom and hence also four possible forms of diamond, which may be designated as  $\alpha\alpha$ ,  $\alpha\beta$ ,  $\beta\alpha$  and  $\beta\beta$  respectively. The first and the last would have true octahedral symmetry, while the second and the third would have the lower or tetrahedral symmetry. The differences in physical behaviour exhibited by even ideal diamonds in various respects, including especially their infra-red absorption spectra, thus receive a natural and intelligible explanation.



# THE VIBRATIONS OF THE MgO CRYSTAL STRUCTURE AND ITS INFRA-RED ABSORPTION SPECTRUM

## Part I. The Results of Experimental Study

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### 1. INTRODUCTION

THE fundamental questions requiring an answer which arise in relation to the infra-red behaviour of crystals are the following: What is the nature of the vibration spectrum of the atomic nuclei in a crystal? How is this vibration spectrum related to its observed infra-red absorption spectra? What is the mechanism of the reflection and of the absorption of infra-red radiation by crystals? A precise and detailed experimental study of the infra-red behaviour of some crystals of simple structure may be expected to furnish an answer to these questions.

Magnesium oxide crystallises in the cubic system and, if the material is pure, the crystals are transparent and colourless. The structure of MgO is similar to that of rock-salt and is thus very simple. Moreover, the binding forces between the atoms being much stronger and their reduced mass much smaller for MgO than for NaCl, the infra-red absorption of MgO appears in a region much more readily accessible to precise investigation than that of rock-salt. Hence, MgO would be a most appropriate choice of material for a study of the kind referred to above.

A collection of MgO crystals came into the writer's hands many years ago as a gift from the Norton Company of Worcester, Mass., U.S.A. Somewhat later, a single crystal of large size was received by him from A. D. Mackay, Inc. of Broadway, New York. It had long been the intention of the writer to make use of this material for a thorough investigation of the kind envisaged in the foregoing paragraphs. Only recently, however, has the availability at this Institute of an infra-red recording spectrograph by Messrs. Leitz of Wetzlar provided with both NaCl and KBr optics enabled



this desire to be fulfilled. The results of the experimental study made with this instrument are described and discussed in this first part of the memoir. In the subsequent parts of the memoir, their theoretical implications and their further consequences are worked out.

The reflecting power of a freshly cleaved surface of an MgO crystal relative to an aluminium mirror was determined by Burstein, Oberly and Plyler (1948) for the spectral region between  $10\mu$  and  $35\mu$  and the results were presented in a paper published in these *Proceedings* some years ago (*Proc. Ind. Acad. Sci.*, 1948, **28 A**, 388). The same authors also recorded the transmission of infra-red radiation in the wavelength range between  $5\mu$  and  $13\mu$  of five cleavage plates of MgO of thicknesses ranging from 9.2 to 0.9 mm. Graphs showing these five transmission curves (in part) and grouped together were reproduced as a figure in the same paper. As regards the reflecting power of MgO, the work of Burstein, Oberly and Plyler was complete and their results will be made use of and discussed in the present memoir. The position is rather different with reference to their studies of the transmission through MgO. Their work did not reveal all the significant features of the behaviour of MgO in this respect. A full and complete picture of the facts is clearly necessary before it is possible for their real significance to emerge. It was with a view to fill the lacunæ in the published results of Burstein, Oberly and Plyler that the present experimental research was undertaken.

## 2. SOME GENERAL CONSIDERATIONS

In the spectrographic investigations with cleavage plates, we are interested in determining the percentage of transmission through the plate and of ascertaining the spectral composition of the transmitted radiation and the manner in which it varies with the thickness of the plate. The loss in transmission may be divided into three parts: (a) the loss by reflection at the surface of incidence, (b) the loss by absorption within the material and (c) the loss by reflection at the surface of emergence. The relative proportions of these three losses would evidently vary with the circumstances, including especially the thickness of the plate, as this would determine the magnitude of the true absorption loss. When the reflecting power is large, the three losses would add up and it would become difficult to extricate them from each other and evaluate them separately.

At wavelengths greater than  $13\mu$ , the reflecting power of MgO is small, as was shown by Burstein, Oberly and Plyler and its alteration with



wavelength would therefore not be significant. Hence in the spectral region between  $5\mu$  and  $13\mu$  covered by their studies of the transmission by MgO, the interpretation of the observations presents no particular difficulty. The position is, however, different in the wavelength range between  $13\mu$  and  $15\mu$  in which the reflecting power was shown by Burstein *et al.* to rise steeply from nearly zero to 75%. This rapid increase would make it difficult to determine how the absorption loss within the material varies with wavelength in the same range. However, by making observations with different thicknesses, the existence of a true absorption could be demonstrated. The position would be much more difficult in the wavelength range between  $15\mu$  and  $25\mu$ . The reflecting power in this range is very high and hence the percentage transmission would be small and difficult to determine, unless indeed the plate is itself so thin that the full reflecting power would be unable to manifest itself. Indeed, it is clear that for an elucidation of the infra-red behaviour of MgO in the wavelength range between  $15\mu$  and  $25\mu$ , it would be necessary to work with extremely thin layers of the material, not exceeding a few microns.

A method of obtaining MgO films for the study of their transmission properties which has been frequently employed by the earlier investigators is that of the deposition of the fumes of burning magnesium on a plate transparent to infra-red radiation. It will suffice here to refer to the work of A. O. Momin published in these *Proceedings* in which references to the earlier literature will be found (*Proc. Ind. Acad. Sci.*, 1953, 37 A, 254). Momin made a series of measurements with fourteen different thicknesses of MgO films prepared by fuming on to a KCl plate from a burning magnesium ribbon. Commencing with an extremely thin layer which was just visible, the thickness was progressively increased by adding more layers of MgO on the same plate by fuming up to a thickness of about 2.4 millimetres when the films begin to break away from the KCl plate. The readings were taken with a single-beam Beckman Model IR 2 infra-red spectrophotometer making point-to-point observations. Four typical graphs which between them cover the whole range of thicknesses employed have been reproduced with Momin's paper. They show some interesting features, but it is quite clear on an inspection of the graphs that they do *not* represent the real transmission curves of MgO at any of the thicknesses used and that on the other hand they depict a complex effect in which the scattering of infra-red radiation in its passage through the optically heterogeneous film produced by the deposition of the fumes and the extinction produced by such scattering play a highly important role.



The spurious and misleading nature of the results given by fumed films of MgO becomes evident when it is remarked that to exhibit an observable transmission in the wavelength range between  $15\mu$  and  $25\mu$ , the thickness of the film cannot exceed a few microns. Films of this order of thickness should be fully transparent in the wavelength range between  $1\mu$  and  $13\mu$ . Actually, Momin's graph for his thinnest film shows a transmission of only 17% at  $1\mu$ . This increases fairly rapidly to 70% at  $5\mu$  and then more slowly to 80% at  $13\mu$ . The optical heterogeneity of the film has thus a notable effect on its transmission up to  $13\mu$ . Hence, to assume that it would cease to influence the behaviour of the film at still greater wavelengths is clearly unjustifiable. The falsity of the assumption is demonstrated by the comparative studies made at this Institute with fumed MgO films and with two other techniques presently to be described. The publications by earlier investigators who have based themselves and their theoretical discussions on the results obtained with fumed MgO films are vitiated by this error and are therefore entirely valueless.

### 3. METHODS OF THE PRESENT INVESTIGATION

Since MgO crystals exhibit an easy cleavage parallel to the cube faces, it is possible to obtain a whole series of plates suitable for the observation and of various thicknesses ranging from several millimetres down to about a tenth of a millimetre. It is desirable to use a fairly large crystal to start with. The area of the plates detached from it would then be sufficient to make a satisfactory recording of the transmission curves. The cleavage surfaces are not always optically as smooth as could be desired. It is necessary in such cases to grind and polish both the faces to as high a degree of optical perfection as practicable. To obtain plates thinner than about a tenth of a millimetre, two alternative techniques are available. That employed in the present investigation was to grind and polish both faces of a cleavage plate about a millimetre thick to start with and having made observations with it, to grind one of the faces with the finest grade of carborundum abrasive until the thickness is reduced to the extent desired. The ground face is then repolished and the transmission recorded. This process can be repeated and the transmission by plates which are progressively thinner and thinner can be studied until the practical limit to the applicability of the method is reached. This limit is set by the fragility of the material. With plates of fair size, it is possible to reduce the thickness to about 50 microns, while with smaller sizes one can go down to about 20 microns.



An alternative technique is to immerse a cleavage plate in hot concentrated hydrochloric acid and allow the acid to act until the thickness of the plate has been reduced to the desired extent. The defect of this technique is the unsatisfactory nature of the resulting surfaces.

To obtain the extremely thin absorption layers with which one could expect to find an observable transmission in the spectral range between  $15\mu$  and  $25\mu$ , the following technique was adopted in the present investigation. A small fragment of an MgO crystal was reduced to the finest possible state of subdivision by prolonged grinding in an agate mortar. A little of the material thus obtained was stirred up into a thin paste with liquid paraffin. The transmission in the KBr range of the spectrograph by the thinnest possible layer of this paste held between two KBr plates was recorded, the absorption by the paraffin being compensated by a similar layer of the liquid alone held between two KBr plates. As a test of the satisfactory nature of the technique, the transmission in the NaCl range was also recorded.

Another technique which was also adopted was to mix a very small quantity of very finely divided MgO with one gram of finely powdered KBr and to compress the MgO-KBr mixture under high pressure in a vacuum into a flat tablet of which the transmission was recorded. By varying the quantity of MgO which was put into the tablet, the effective absorption path could be increased to the extent desired.

Since the paste and pellet techniques gave very similar results, it was not considered necessary to try out still another possible procedure of obtaining thin films of MgO, *viz.*, that of evaporating the material in a vacuum and depositing it on a suitable support.

#### 4. REVIEW OF THE RESULTS

The wavelength scale of the recording spectrograph for the NaCl optics covers the range between  $1\mu$  and  $15\mu$ , while with the KBr optics it covers the range between  $13\mu$  and  $24\mu$ . The overlap of the two scales over the range between  $13\mu$  and  $15\mu$  is a useful feature, since it provides a check on the proper functioning of the instrument and as it is also the range over which the reflecting power of MgO increases rapidly from nearly zero to some 75%.

Some 75 spectrographic records were made with the instrument, the majority with the NaCl optics and the rest in the KBr range. Some 25 different cleavage plates of various sizes and thicknesses were employed and numerous records were also obtained with the paste and pellet techniques.



already described. Before we proceed to discuss the results in detail, it appears useful to review the general features which emerge from the study, thereby enabling us to get a broad picture of the experimental situation and consider its significance.

The most striking feature exhibited by the records is that the infra-red behaviour of MgO is quite different in the three spectral ranges which we shall refer to as I, II and III respectively. Spectral range I extends from  $6\mu$  to  $10\mu$ . Spectral range II extends from  $10\mu$  to  $15\mu$ . Spectral range III extends from  $15\mu$  to  $24\mu$ . Closely associated with this feature is the fact that the spectral character of the radiation transmitted by MgO depends greatly upon the absorption path. When the cleavage plate is a few millimetres thick, spectral region I exhibits a progressive change from complete transparency at  $6\mu$  to complete opacity at  $10\mu$ , while spectral regions II and III are completely cut out. If the absorption path is a few tenths of a millimetre, spectral range I is almost completely transmitted and spectral region II exhibits a transmission spectrum with characteristic features, while spectral region III is cut out. If the absorption path is only a few microns, spectral range III exhibits an observable transmission, while spectral region I, is completely transmitted and spectral region II is let through for the most part.

The facts stated above clearly indicate that the infra-red activities which manifest themselves respectively in the spectral regions I, II and III are of very different orders of magnitude. An explanation for this situation which suggests itself is that the same fundamental modes of vibration are responsible for the activities manifested in the three spectral regions, but that we are concerned with the fundamental modes and with their first and their second overtones respectively in the three cases. In other words, the fundamental absorption frequencies manifest themselves in spectral region I, their first harmonics in the spectral region II and their second harmonics in spectral region III. On this basis, the great differences in the strength of the observed absorptions in the three regions would find an immediate explanation.

If what has been suggested above is correct, we should expect to find quantitative relationships between the specific features observed in the spectral regions I, II and III in the recorded transmission curves. We proceed, therefore, to describe and discuss these observed features.

##### 5. SPECTRAL REGION I: $6\mu$ TO $10\mu$

We may begin with a few remarks on the transmission of infra-red radiation in the wavelength range between  $1\mu$  and  $5\mu$  by cleavage plates



of MgO. Residual imperfections in the cleavage surfaces are unavoidable. Their effect manifests itself as a diminution in the percentage of the regularly transmitted radiation in the region of the near infra-red. If, however, a large-sized crystal is used and its cleavage is effected with due care, the effect of surface imperfections on the transmission which may be perceptible at  $1\mu$  becomes small at  $4\mu$  and negligible at  $5\mu$ . Transmissions as high as 95% may be obtained at  $5\mu$ .

The region between  $5\mu$  and  $6\mu$  is of particular interest. With a cleavage plate 7.5 millimetres thick, the transmission is observed to diminish by 8% between  $5\mu$  and  $6\mu$ . With a plate thickness of 3 millimetres, the diminution is only 3%, while with a plate thickness of 1.6 millimetres, there is no observable fall of the transmission between  $5\mu$  and  $6\mu$ , the curve running quite horizontally between these wavelengths. It is clear from these observations that while there is a sensible absorption of infra-red radiation between  $5\mu$  and  $6\mu$ , it is extremely weak and of a lower order of magnitude than the absorption between  $6\mu$  and  $10\mu$  which we shall proceed to describe and discuss.

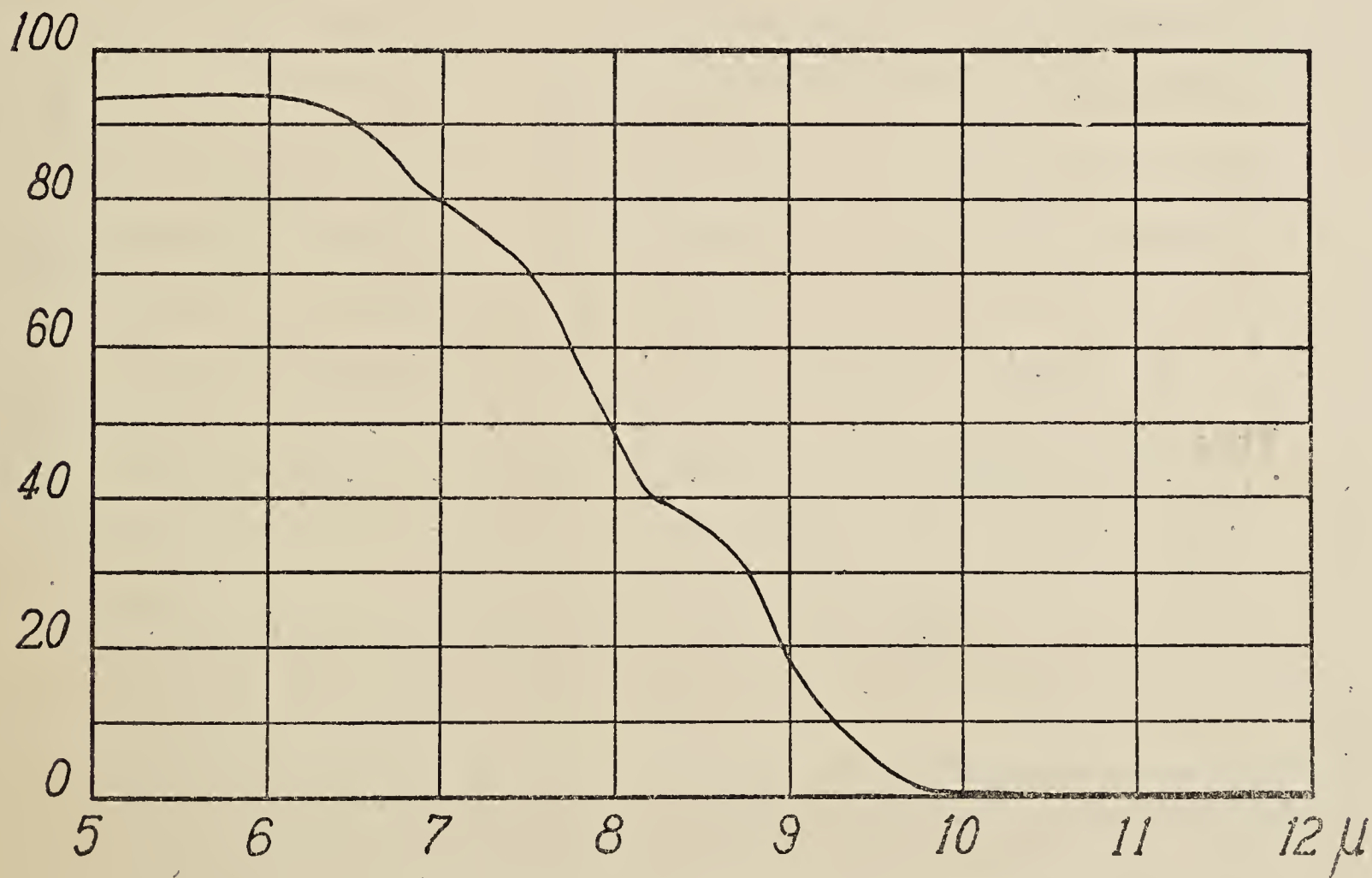


FIG. 1. Transmission by an MgO plate 2.34 mm. thick.

Figure 1 reproduces the record obtained with a cleavage plate 2.34 millimetres thick. We may draw attention here to the following features observed in it. The record runs horizontally between  $5\mu$  and  $6\mu$ . Beyond  $6\mu$ , it dips down and becomes steepest at  $6.8\mu$ . It then takes a sharp turn and



follows a different course in which the wavelength at which the transmission drops most steeply is  $7.85\mu$ . Between  $8\mu$  and  $9\mu$  the curve again changes its course. The slope is rather small at  $8.5\mu$ , beyond which it increases rapidly. The wavelength of steepest descent is  $9\mu$ . Between  $9\mu$  and  $10\mu$ , the curve descends less quickly. Its slope diminishes until finally the curve touches the line of zero transmission at  $10\mu$ . Beyond  $10\mu$ , there is a complete cut-off.

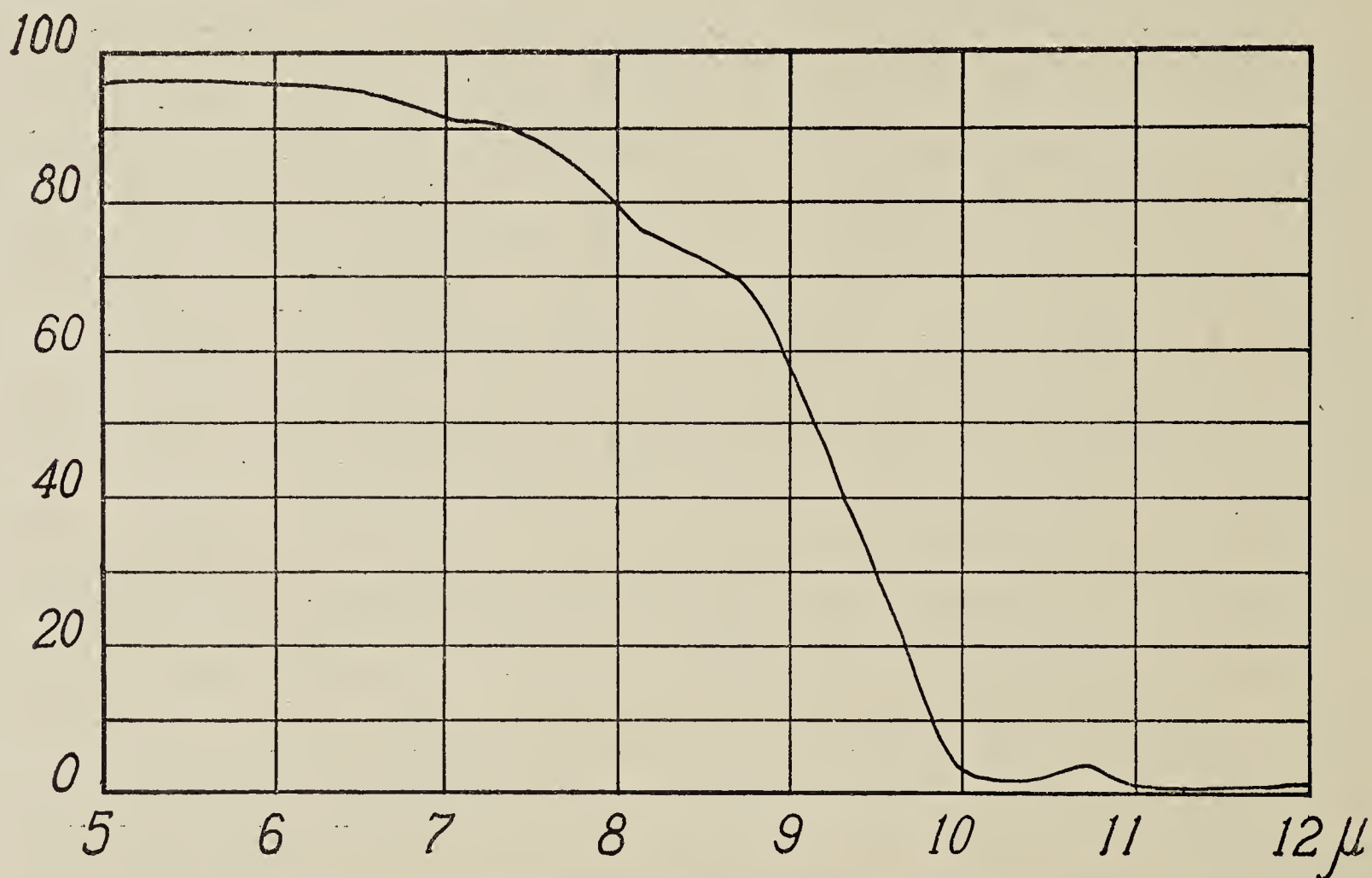


FIG. 2. Transmission by an MgO plate 0.91 mm. thick.

Thus, the spectrographic record of transmission between  $6\mu$  and  $10\mu$  consists of three distinct sectors which exhibit quite different features, the transmission falling most steeply in the three sections at the wavelengths  $6.8\mu$ ,  $7.85\mu$  and  $9\mu$  respectively. The three sectors can also be recognised in numerous other records which have been made with various thicknesses, viz., 7.5 mm., 3.0 mm., 1.6 mm., 1.34 mm., 1.04 mm. and 1.00 mm. It has, however, not been thought necessary to reproduce all these records here. That the three sectors exhibit the effect of specific absorptions is shown by the fact that each of them has a distinct absorption strength and that this results in altering the over-all configuration of the graph in the wavelength range between  $6\mu$  and  $10\mu$  when the thickness is increased or diminished. Nevertheless, there is no difficulty in recognising the individual distinctive features described above in every case. In particular, the wavelengths of steepest descent, viz.,  $6.8\mu$ ,  $7.85\mu$  and  $9\mu$  remain the same in



all the records. Thus, these wavelengths possess a real significance in relation to the absorptive behaviour of MgO.

The wavelengths  $6.8\mu$ ,  $7.85\mu$  and  $9\mu$  correspond to infra-red frequencies which expressed in wave-numbers are respectively  $1470\text{ cm.}^{-1}$ ,  $1275\text{ cm.}^{-1}$  and  $1110\text{ cm.}^{-1}$ . Assuming these to be the second overtones of a set of fundamentals, the latter would be  $490\text{ cm.}^{-1}$ ,  $425\text{ cm.}^{-1}$  and  $370\text{ cm.}^{-1}$  in wave-numbers and  $20.40\mu$ ,  $23.52\mu$  and  $27.0\mu$  respectively in wavelengths. The first overtones would then have the frequencies  $980\text{ cm.}^{-1}$ ,  $850\text{ cm.}^{-1}$  and  $740\text{ cm.}^{-1}$  in wave-numbers and the corresponding wavelengths would be  $10.20\mu$ ,  $11.76\mu$  and  $13.5\mu$ . The frequencies of the fourth order would be  $1960\text{ cm.}^{-1}$ ,  $1700\text{ cm.}^{-1}$  and  $1480\text{ cm.}^{-1}$  and the corresponding wavelengths  $5.1\mu$ ,  $5.9\mu$  and  $6.8\mu$  respectively. We give below a table of these frequencies and wavelengths.

TABLE I  
*Vibrational frequencies and corresponding wavelengths*

Order	Frequencies in $\text{cm.}^{-1}$	Wavelengths in $\mu$
Fundamental ..	490, 425, 370	20.40, 23.52, 27.0
Octave ..	980, 850, 740	10.20, 11.76, 13.5
Third Harmonic ..	1470, 1275, 1110	6.8, 7.85, 9.0
Fourth Harmonic ..	1960, 1700, 1480	5.1, 5.9, 6.8

The figures listed in Table I enable us immediately to explain various facts already known regarding the infra-red behaviour of MgO. For example, Burstein, Oberly and Plyler had observed that the reflecting power of MgO determined and represented graphically is highest in the wavelength region between  $20\mu$  and  $24\mu$ . We notice that this region includes the first two fundamental wavelengths shown in Table I. Then again, Burstein, Oberly and Plyler had noticed that in the transmission curves of MgO plates which were less than a millimetre thick, two well-defined absorption maxima appear whose wavelengths were given by them as  $10.19\mu$  and  $11.82\mu$ . These may be identified as the first two wavelengths of the octave series shown in Table I. The fact mentioned earlier in the present memoir, that there is an extremely weak infra-red absorption between  $5\mu$  and  $6\mu$  is also satisfactorily explained, since the first two wavelengths shown as the fourth harmonics in Table I fall within this range.



Thus, what is already known regarding the infra-red behaviour of MgO provides us with ample justification for accepting the basic idea which was put forward above and making use of it in interpreting the fresh experimental data which emerge from the present investigation.

#### 6. SPECTRAL REGION II: $10\mu$ TO $15\mu$

That the infra-red absorption appearing between  $6\mu$  and  $10\mu$  is of a higher order than that manifested between  $10\mu$  and  $15\mu$  is clearly proved by various facts of observation. In the first place, there is a total cut-off between  $10\mu$  and  $15\mu$  unless the absorption paths are used are much smaller than those which are required to exhibit any sensible absorption in the  $6\mu$  to  $10\mu$  region. Then again, when such smaller thicknesses are used, the transmission is observed to be nearly complete over the range between  $6\mu$  and  $10\mu$ ; in these circumstances also, a steep fall is observed in the transmission curve near  $10\mu$  which is the dividing boundary between spectral ranges I and II (see Figs. 2, 3, 4 and 5).

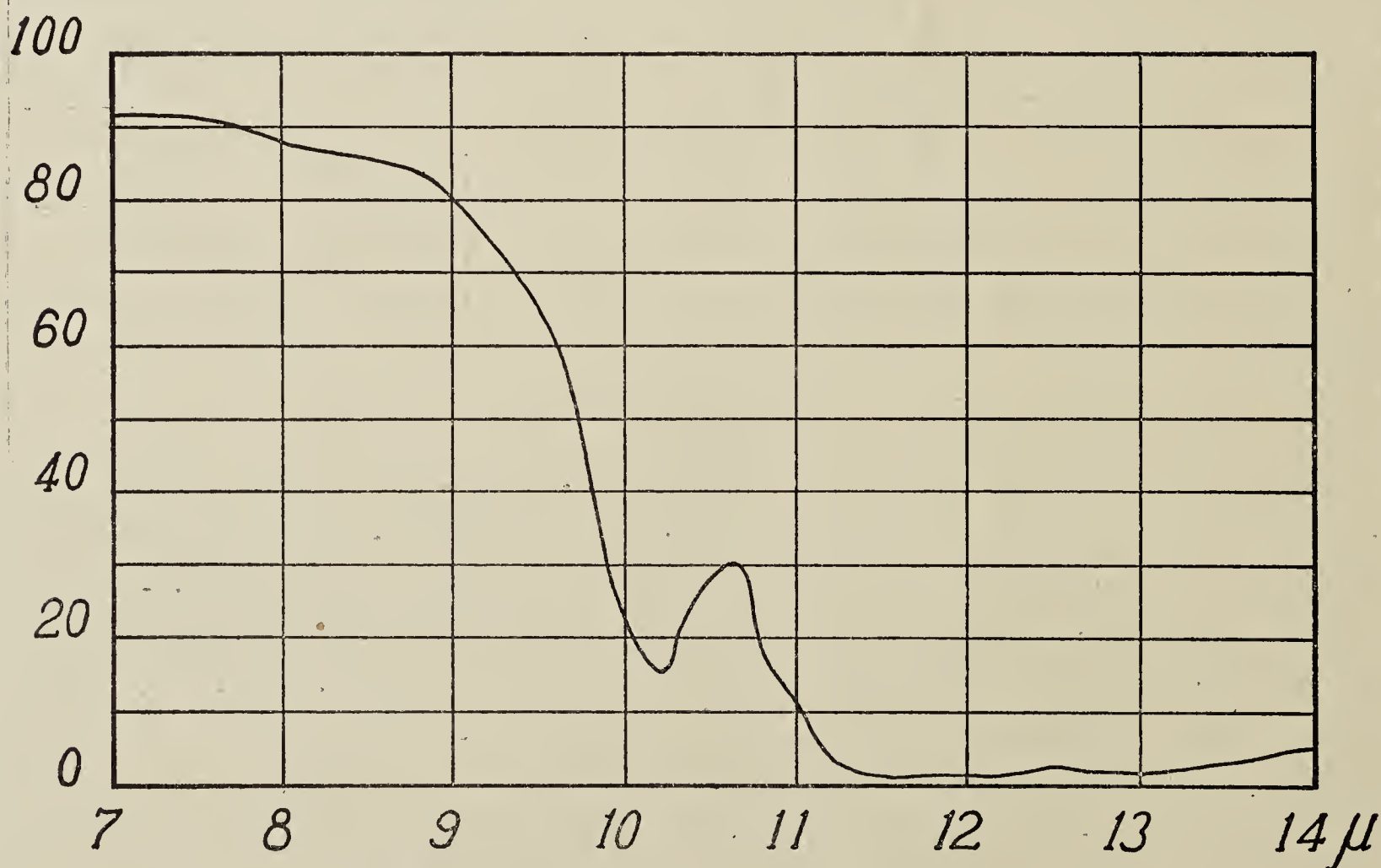


FIG. 3. Transmission by an MgO plate 0.30 mm. thick.

On the long-wave side of the boundary between spectral regions I and II, the characteristic absorption at  $10.20\mu$  first clearly makes its appearance when the absorption path is rather less than one millimetre. This absorption evidently represents the octave of the highest fundamental frequency of vibration of the crystal structure of MgO. As the absorption path is



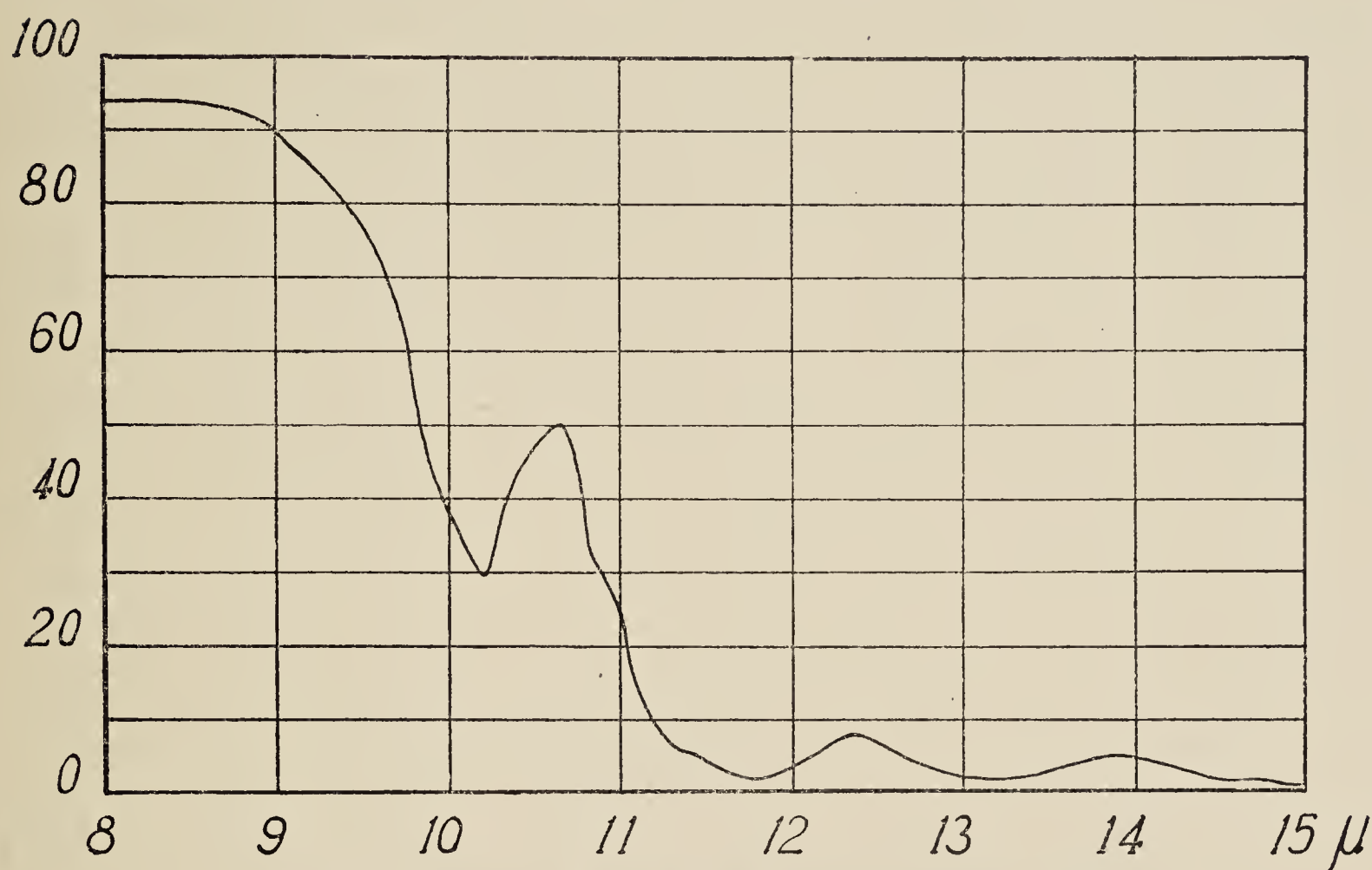


FIG. 4. Transmission by an MgO plate 0.128 mm. thick.

progressively diminished, this absorption emerges more and more clearly from its background and become a very striking feature of the transmission curves. Its initial appearance is shown in Fig. 2 which was recorded with a cleavage plate 0.91 mm. thick. A later stage in which the absorption at  $10.20\mu$  is very prominent and exhibits its characteristic sharpness and V-shaped configuration is represented in Fig. 3 above recorded with a cleavage plate 0.30 mm. thick. With diminishing thickness of the plate, the V-shaped dip in transmission retains both its sharpness and its position on the wavelength scale at  $10.20\mu$  but moves upwards in the figure, as is to be expected from the diminishing strength of the absorption which it represents (see Figs. 4, 5, 6, 7, 8 and 9).

The second minimum of transmission located at  $11.76\mu$  and shown in Table I as an octave of a fundamental mode makes its appearance rather inconspicuously in Fig. 3. But as the thickness of the plate is progressively diminished, it becomes more and more conspicuous, as will be seen from the series of records, until it becomes even more conspicuous than the minimum at  $10.20\mu$  (Figs. 4, 5, 6, 7 and 8). Like the minimum at  $10.20\mu$ , the minimum at  $11.76\mu$  retains its position on the wavelength scale but moves upwards as the absorption path is diminished.

Referring to the spectrographic records reproduced as Figs. 4, 5 and 6, we find that in each of them, the transmission reaches a maximum at about



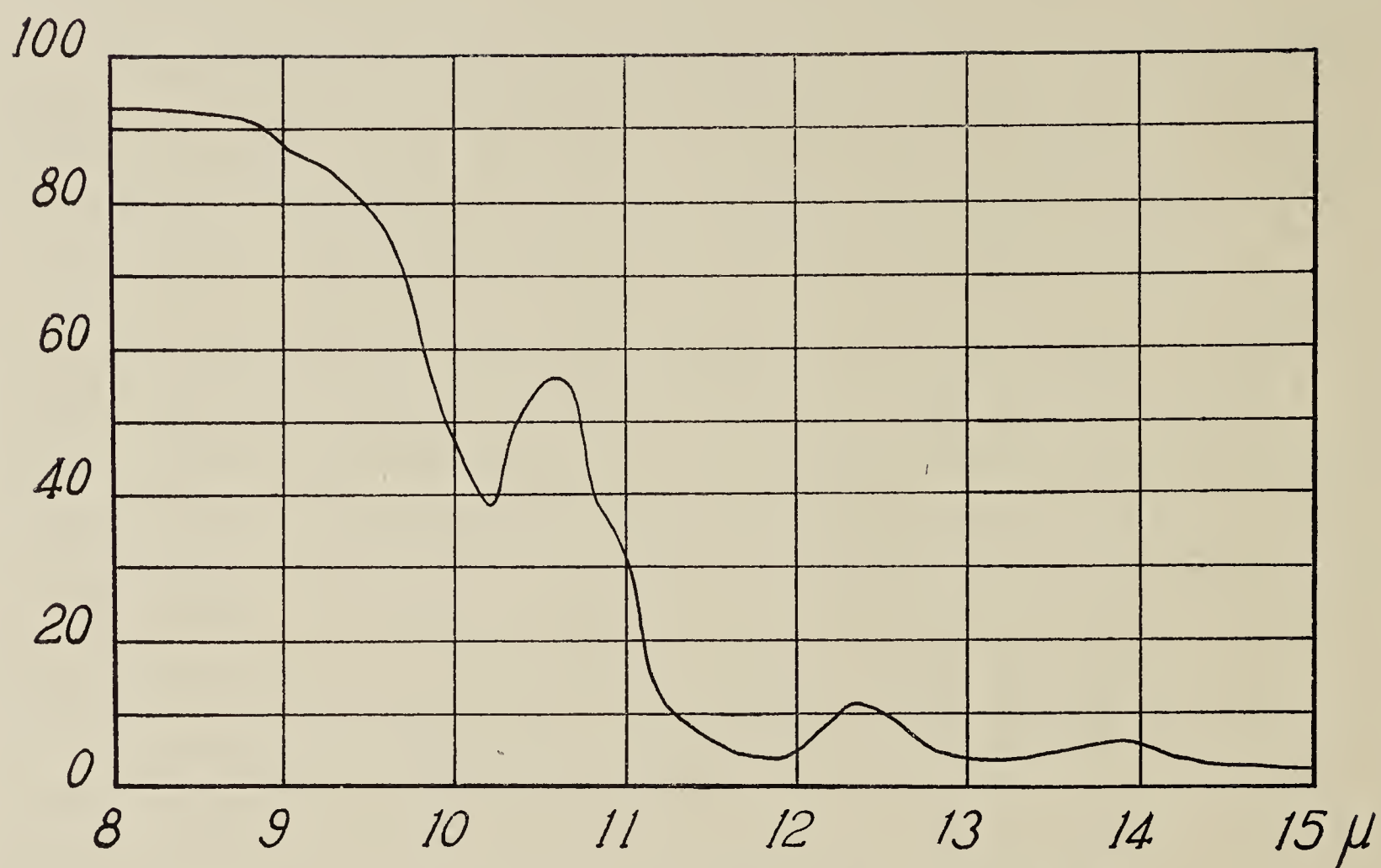


FIG. 5. Transmission by an MgO plate 0.114 mm. thick.

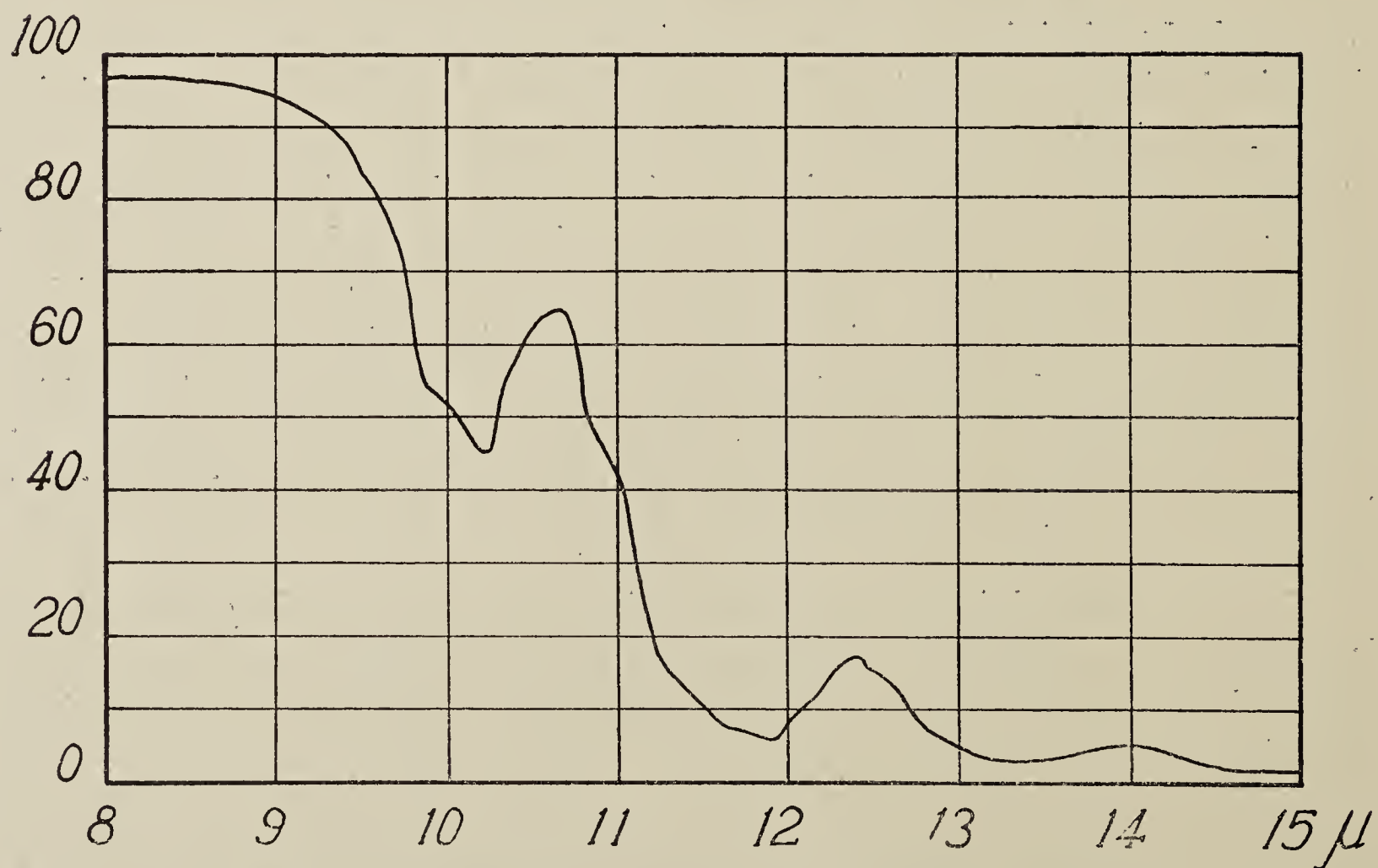


FIG. 6. Transmission by an MgO plate 0.088 mm. thick.

12.4  $\mu$  and then drops down to a much lower value at about 13.3  $\mu$ . The actual transmission at 13.3  $\mu$  is small in Fig. 4 and is distinctly larger in Figs. 5 and 6. That there is a real absorption at 12.4  $\mu$  and that this goes



up to a much higher value at  $13.3\mu$  is thus abundantly clear. We are therefore justified in stating that there is a minimum of transmission at about the wavelength  $13.5\mu$  which was listed in Table I as the third in the series of octaves. The reason why the existence of this minimum is not made more conspicuous by a progressive rise of the curve in the region between  $13.5\mu$  and  $15\mu$  with diminishing thickness is to be found in the enormous increase in the reflecting power of MgO which occurs in the same region of wavelength. The fall in transmission arising therefrom more than sets off the increase in the transmission due to the diminishing thickness of absorbing material.

That the percentage transmission through a plate of MgO in the wavelength region between  $13.7\mu$  and  $15\mu$  is almost entirely determined by the reflection losses is evident on a comparison of the records for this region appearing in Figs. 8 and 9 below. The absorbing path in the two cases was respectively 57 microns and 21 microns. It will be noticed that in spite of this great difference in the thickness of the absorbing material, the percentage transmission between  $13.7\mu$  and  $15\mu$  remains substantially unaltered, whereas between  $12\mu$  and  $13.7\mu$ , it has increased enormously.

Thus, the inference from the observations made in spectral region I that three absorptions which we now locate at  $10.20\mu$ ,  $11.82\mu$  and  $13.7\mu$  respectively should appear in spectral region II is abundantly confirmed by the actual facts of observation. The conclusion follows irresistibly that the MgO crystal structure has the three fundamental modes of vibration with the respective frequencies which have been listed in Table I.

#### 7. SPECTRAL REGION III: $15\mu$ TO $24\mu$

The techniques used to study the transmission in this region using the KBr optics have already been explained. Figure 10 shows two transmission records obtained with the paste technique: the upper of the two curves was obtained without any spacer to hold apart the two KBr plates between which the thin film of paraffin containing the finely divided MgO was located. The thickness of the film was hence the very smallest possible and presumably of the same order of magnitude as the size of the MgO particles contained in it. The second record in the figure was with a spacer 30 microns thick separating the two KBr plates. The two records reproduced in Fig. 11 are those recorded with NaCl optics for the wavelength region between  $8\mu$  and  $15\mu$  in the same two cases. We shall return presently to a consideration of the features appearing in Figs. 10 and 11.



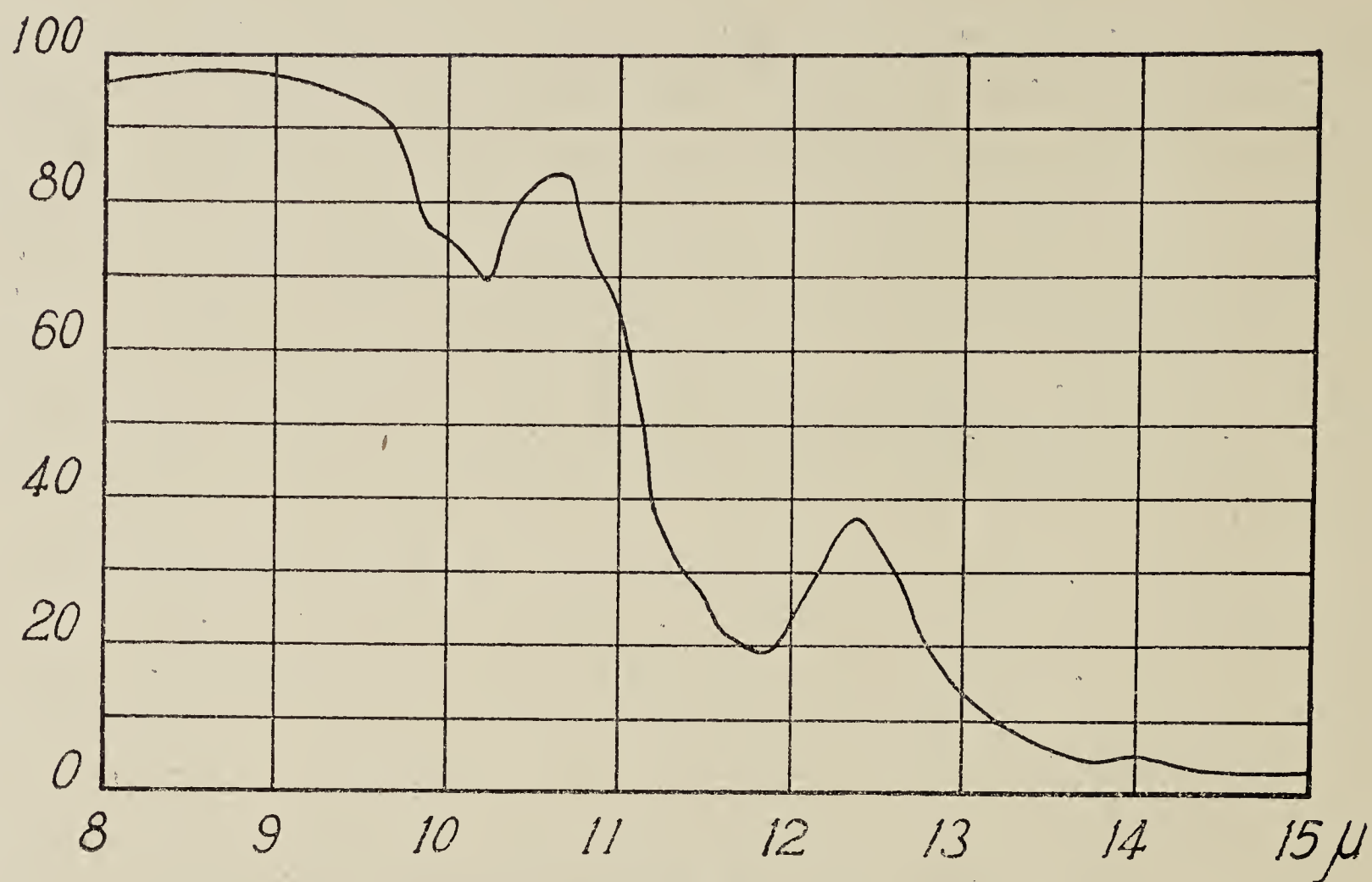


FIG. 7. Transmission by an MgO plate 0.06 mm. thick.

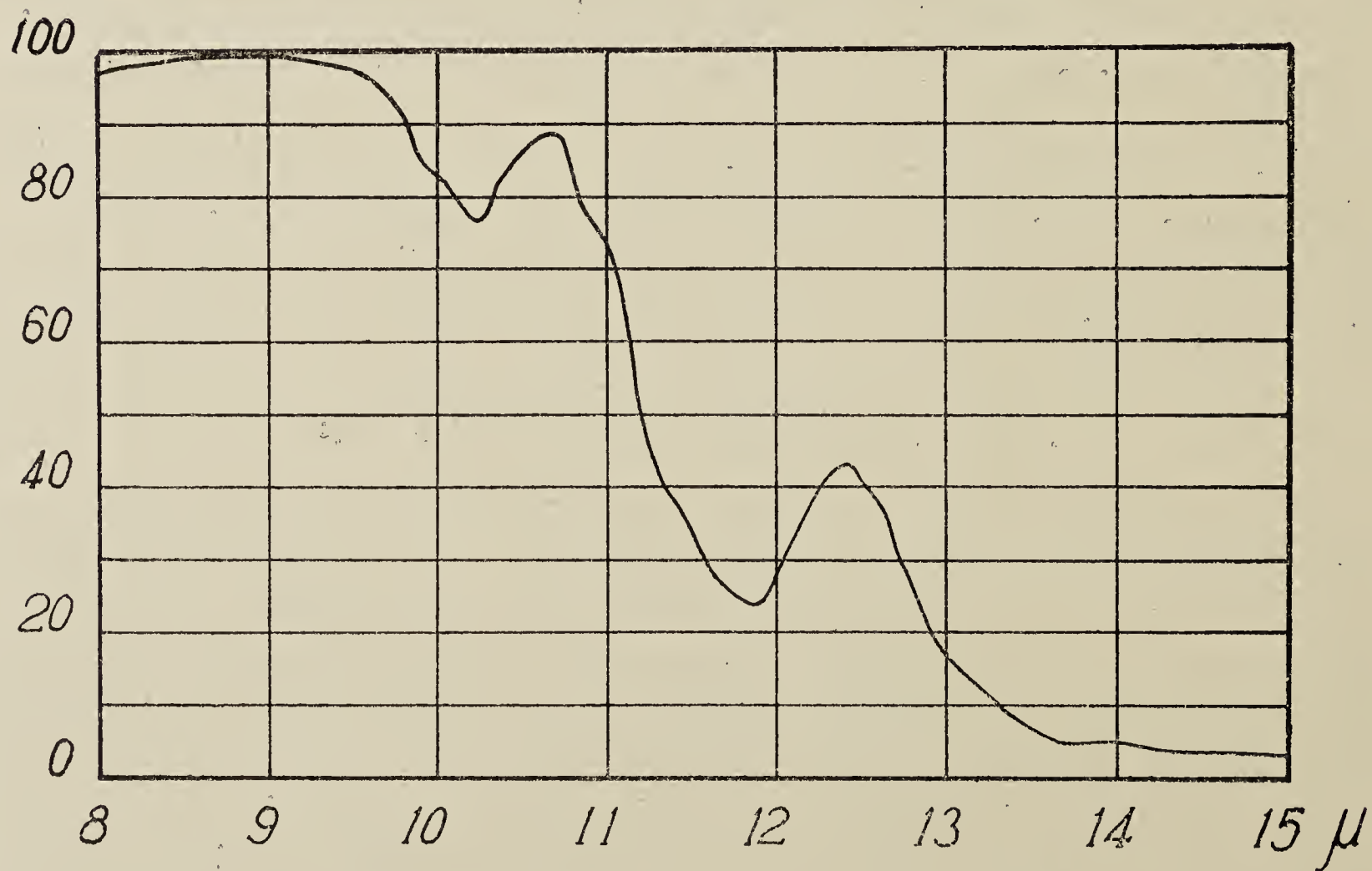


FIG. 8. Transmission by an MgO plate 0.057 mm. thick.

Figure 12 below reproduces four records for the KBr range of the spectrograph obtained with the pellet technique already described. The pellet was a circular disc of 1 centimetre radius containing one gram of KBr and



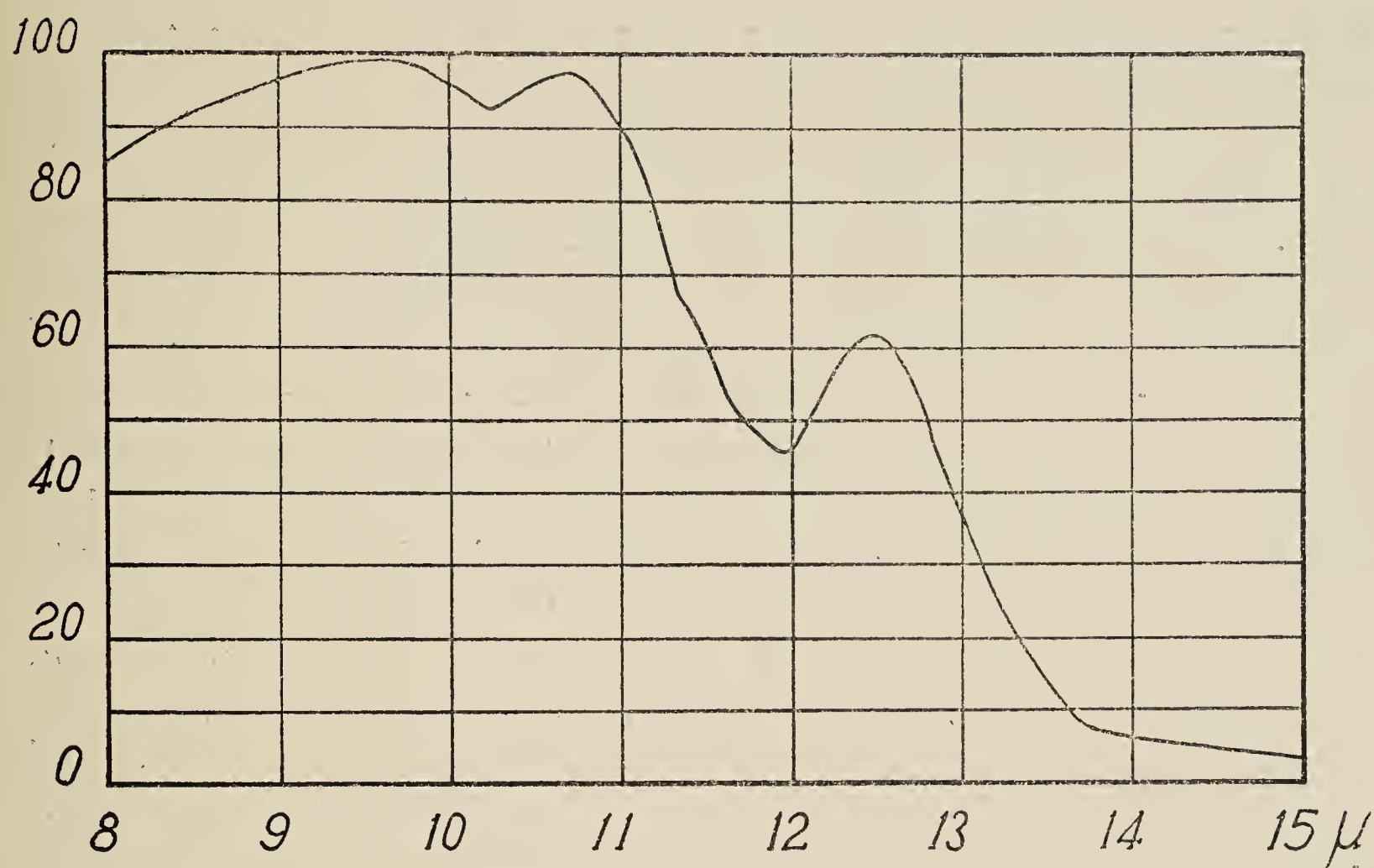


FIG. 9. Transmission by an MgO plate 0.021 mm. thick.

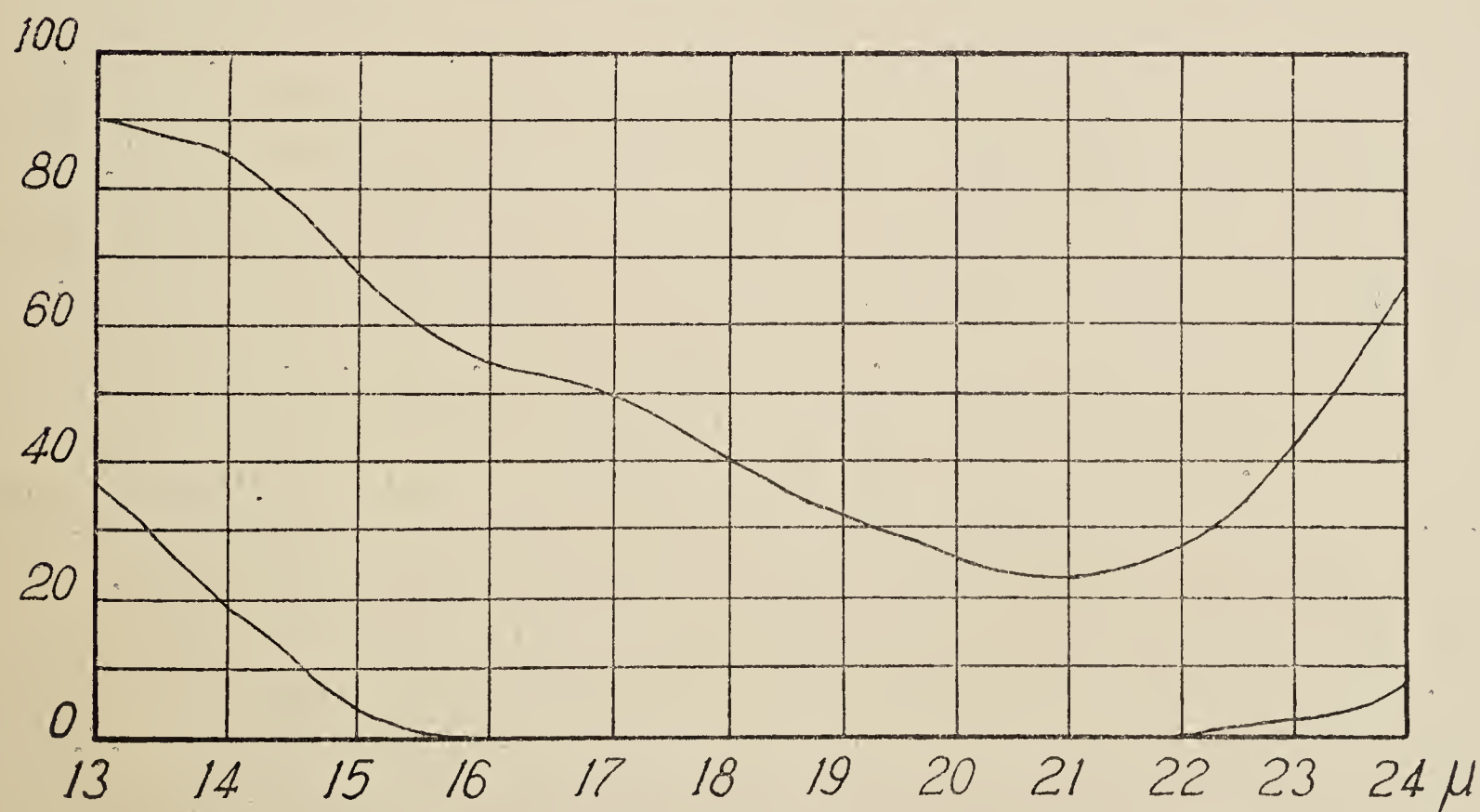


FIG. 10. Transmission curve of MgO films (Paste Technique).

four different quantities of finely divided MgO, viz., 1 milligram, 1.2 milligrams, 2 milligrams and 5 milligrams respectively. The effective absorption paths through MgO would thus be respectively in the four cases  $3.2\mu$ ,  $3.8\mu$ ,  $6.4\mu$  and  $16\mu$ . As is to be expected, the four figures exhibit a rapid and



progressive change as the effective thickness of the MgO layer is increased.

We may make the following remarks on the data presented in Figs. 10, 11 and 12. It is evident that the results obtained with the two different techniques are very similar and that they fit into each other perfectly when the differences in the effective absorption paths are taken into consideration. Indeed, the curves in Figs. 10 and 12 form a regular sequence showing how the transmission alters with a progressive increase in absorption path. The upper curve in Fig. 10 represents the behaviour of the thinnest possible layer; the first three curves in Fig. 12 represent the subsequent alterations with increasing thickness, while the second curve in Fig. 10 and the fourth curve in Fig. 12 represent the final stages in which the layers are practically opaque to all radiations in the wavelength region between  $15\mu$  and  $24\mu$ .

The first of the two curves reproduced in Fig. 10 is particularly important. It depicts the absorptive behaviour of an MgO film when it is so thin that the losses due to reflection at its two surfaces can be disregarded. It is significant that the absorption is greatest at about  $21\mu$  and falls off quickly at greater wavelengths. This is the behaviour which we might expect to observe if the fundamental mode of highest frequency of which the characteristic wavelength is  $20.40\mu$  is the only mode which is infra-red active, while that the numerous other modes whose characteristic wavelengths are larger and have been listed in Table I are either totally inactive or active only in a very minor degree. The shift of the maximum from the theoretical value  $20.40\mu$  to the observed value of  $21\mu$  is readily understood on that basis.

The two curves reproduced in Fig. 11 are also highly significant. They show that the films studied were completely transparent at  $8\mu$ . The two upper curves in Fig. 10 and in Fig. 11 respectively agree in showing a transmission of 90% at  $13\mu$  while the two lower ones similarly agree in showing a transmission of 35% at  $13\mu$ . The transparency of the films at  $8\mu$  is an indication that the losses due to scattering at all greater wavelengths are negligible. In other words, it is a demonstration of the satisfactory nature of the technique employed. In this respect, the results provide a very striking contrast with the behaviour of fumed MgO films. As has already been remarked, the fumed MgO films exhibit the effect of scattering very markedly. Hence the results obtained with them are erroneous and totally misleading.

We may also remark on a feature shown by the upper curve in Fig. 10 and also by the two upper curves in Fig. 12, viz., the downward bulge of the transmission curve in the region of wavelengths between  $15\mu$  and  $17\mu$ .



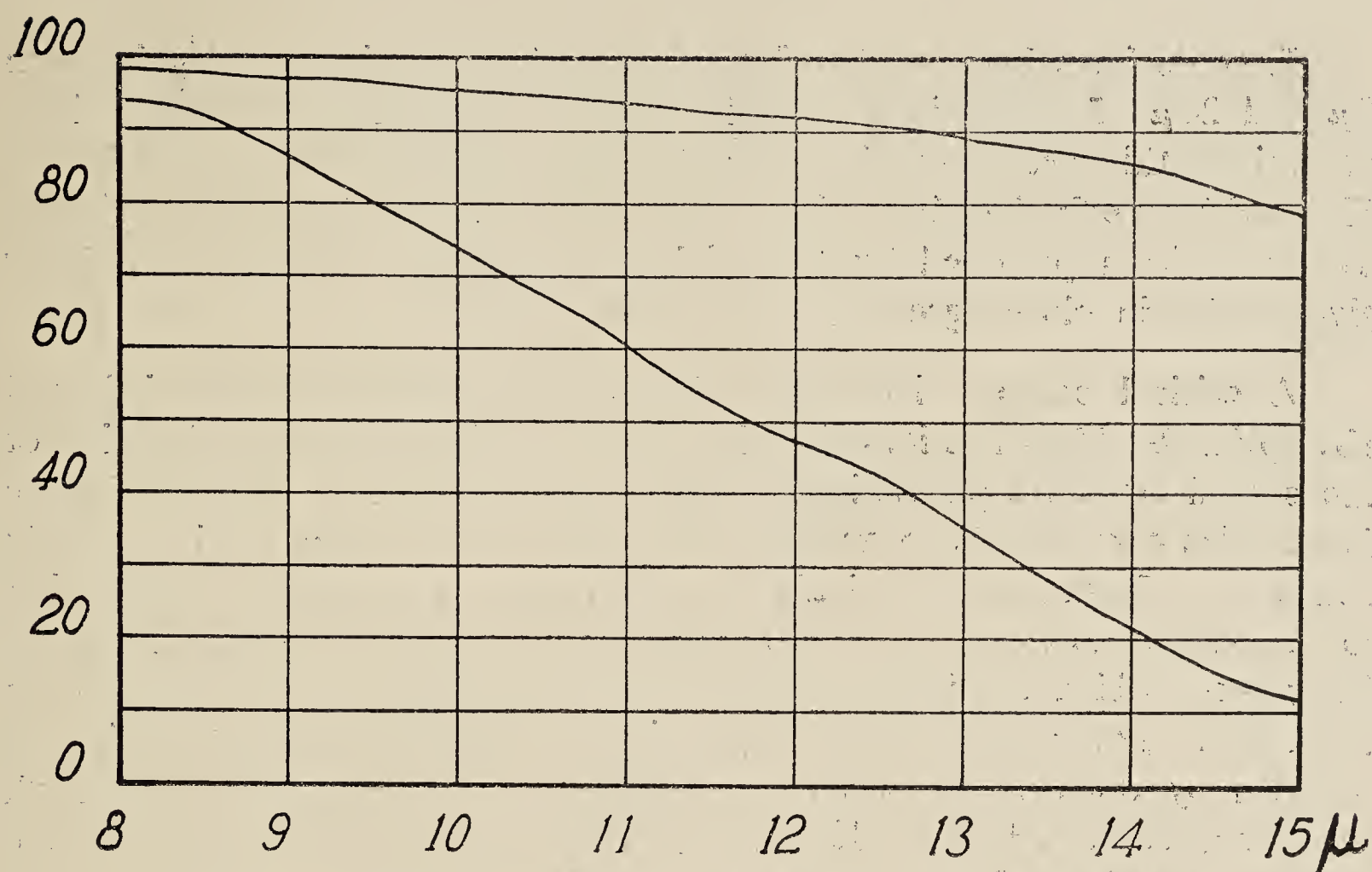


FIG. 11. Transmission curve of MgO films (Paste Technique).

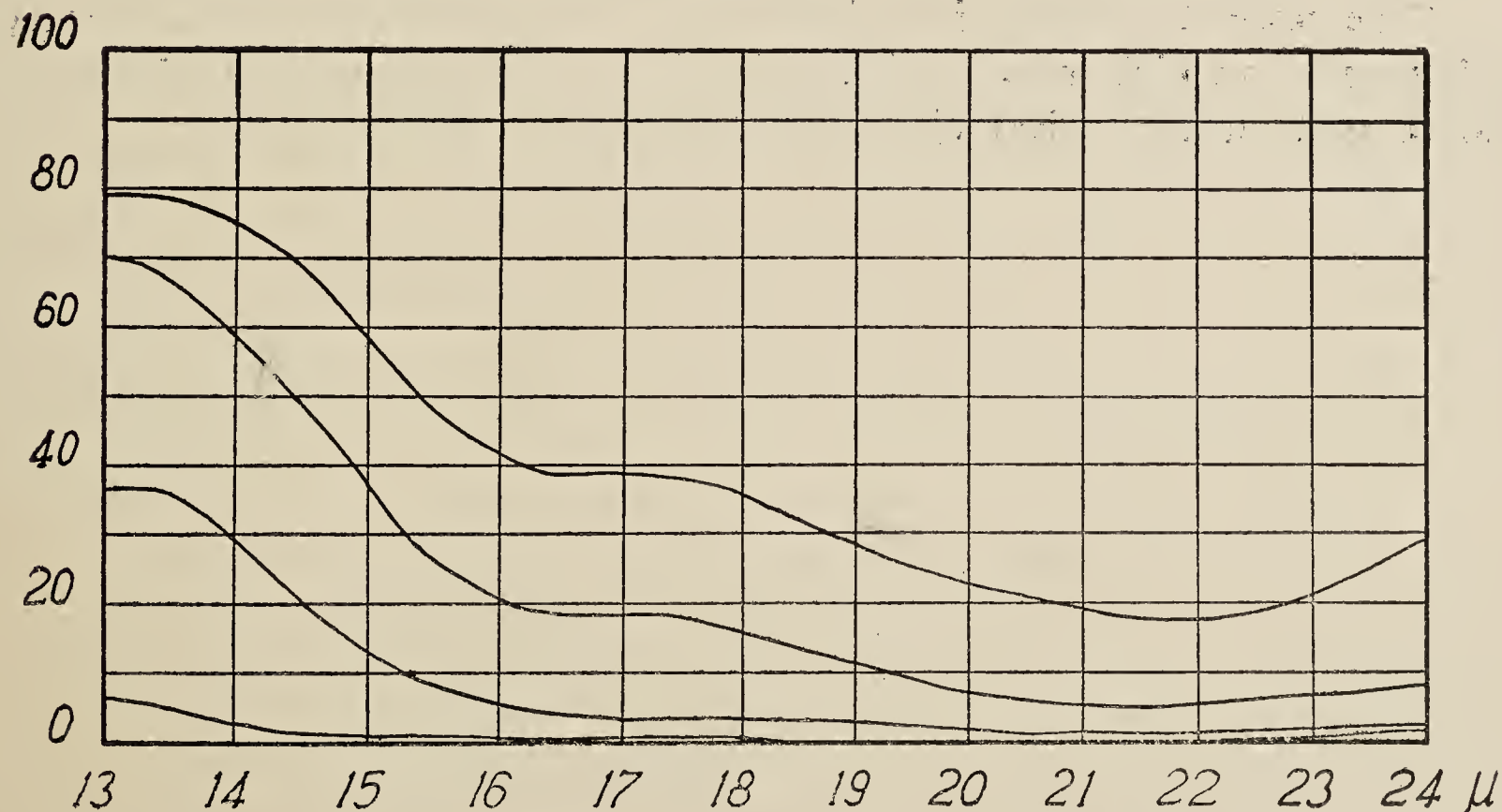


FIG. 12. Transmission curve of MgO films (Pellet Technique).

This is a clear indication that there is a specific absorption which we shall locate at  $16\mu$  and which is clearly the octave of still another fundamental mode whose characteristic wavelength is  $32\mu$  and characteristic frequency is therefore  $313\text{ cm.}^{-1}$



## 8. SUMMARY

Records have been made of the infra-red absorption spectra between  $5\mu$  and  $24\mu$  of magnesium oxide in the form of polished cleavage plates of various thicknesses ranging from 7.5 millimetres down to 20 microns. Films with an effective absorption path ranging from 1 micron to 16 microns have also been prepared by two different techniques and studied. They give results in close agreement with each other.

A critical comparative study of the data reveals that the infra-red absorption by MgO has its origin in a set of distinct modes of vibration of the crystal structure possessing discrete frequencies. The highest of these frequencies corresponds to an infra-red wavelength  $20.40\mu$ . It is strongly active as a fundamental and also as overtones. The infra-red absorption spectra enable us to recognize the presence of three other modes with lower frequencies which are inactive as fundamentals but are strongly active as overtones. The characteristic frequencies of MgO (including the highest) revealed by the investigation are respectively in wave-numbers  $490\text{ cm.}^{-1}$ ,  $423\text{ cm.}^{-1}$ ,  $365\text{ cm.}^{-1}$  and  $313\text{ cm.}^{-1}$ . The corresponding wavelengths are  $20.40\mu$ ,  $23.64\mu$ ,  $27.4\mu$  and  $32\mu$ .

The present investigation shows that the results reported earlier by other authors which were obtained with fumed MgO films are spurious and hence that all theoretical discussions based thereon are valueless.



# THE VIBRATIONS OF THE MgO CRYSTAL STRUCTURE AND ITS INFRA-RED ABSORPTION SPECTRUM

## Part II. Dynamical Theory

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### 1. INTRODUCTION

THE fundamental property of the atomic structure of a crystal is that it comes into coincidence with itself following a unit translation along any one of the three axes of the lattice. Hence the normal modes of atomic vibration characteristic of the structure of a crystal should satisfy a similar requirement, in other words, they should remain unaltered following such a unit translation. From this, it follows that the atomic modes of vibration satisfy the following rule: in any normal mode, equivalent atoms in the structure have *either* the same amplitude and the same phase, *or* the same amplitude but alternating phases, along the axes of the lattice. In the MgO structure, we have two interpenetrating face-centred cubic lattices of Mg and O atoms respectively. Applying the rule stated, it should be possible to deduce the normal modes of vibration of this structure purely from symmetry considerations. One could also go further and obtain explicit formulæ for the frequencies of the normal modes in terms of the interatomic force-constants. We shall, in what follows, carry out the programme here indicated.

### 2. VIBRATIONS OF A FACE-CENTRED CUBIC LATTICE

The three unit translations in a face-centred cubic lattice are parallel to the three edges of the primitive rhombohedral cell of the lattice. These edges are found by joining an atom at a cube corner with the three atoms at the centres of the three adjoining cube faces. The various modes of normal vibration of the lattice given by the rule stated above are found by choosing one or another of the eight possible combinations of the phases of these three atoms relative to the phase of the atom at the cube corner and continuing the scheme to the more distant atoms in the lattice. It is then found that the possible modes of vibration may be described *either* as movements of the cubic planes of atoms in the crystal *or* as movements of the



octahedral planes of atoms; in either case, the alternation of phase along an axis results in the alternate planes of one or the other species moving in opposite phases. Since we have three sets of cubic planes and four sets of octahedral planes, the movements of these planes normal to themselves would give three and four normal modes respectively, but only two distinct frequencies. We have also to consider the movements of the planes parallel to themselves, and as there are two possible directions of movement in each case, we obtain six and eight such normal modes respectively, but here again only two additional frequencies by reason of the symmetry of the crystal. Thus, in all, we have only four distinct frequencies of vibration. In the foregoing we left out of consideration the case in which the phases of movement of the three atoms at the face-centres and of the atom at the cube corner are the same. This corresponds to a simple translation of the unit rhombohedral cell carrying eight atoms at its corners. The 24 degrees of freedom of movement of these eight atoms are thus distributed as follows amongst the possible movements of the lattice.

TABLE I

	Degeneracy
Vibrations of the cubic planes normal to themselves ..	3
Vibrations of the cubic planes tangential to themselves ..	6
Vibrations of the octahedral planes normal to themselves ..	4
Vibrations of the octahedral planes tangential to themselves ..	8
Translations of the unit cell .. .. .	3
Total degrees of freedom .. .. .	24

### 3. THE VIBRATIONS OF THE MGO STRUCTURE

In the MgO crystal, the Mg and O atoms occupy the points of two similar face-centred cubic lattices interpenetrating each other. These are so disposed that each Mg atom is surrounded by six equidistant O atoms, and each O atom is surrounded by six equivalent Mg atoms. In the cubic planes of the structure the Mg and O atoms appear together, while in the octahedral planes they appear separately but in equidistant planes, each plane of Mg atoms having two planes of O atoms and each plane of O atoms having two planes of Mg atoms situated symmetrically on either side of it.



This arrangement has interesting consequences regarding the possible vibrational modes of the structure, as we shall presently see.

Table I would represent equally well the schemes of vibration of the Mg atoms and of the O atoms. Hence, the interactions of these atoms with each other would result in a modification of the frequencies of vibration without altering the geometry of the modes. Since the cubic planes contain both Mg and O atoms, each of their movements would split into two modes: in one of the two modes, the Mg and O atoms in a cubic plane would oscillate in the same phase and in the other they would oscillate in opposite phases. The situation would be a little different with respect to the atomic layers parallel to the octahedral faces. In view of the disposition of Mg and O atoms in these layers, it is evident that the oscillations of Mg and O layers would occur independently of each other, the Mg planes remaining at rest when the O planes oscillate and *vice versa*. The three translations of the unit cells would also split into two. The movement of the Mg and O atoms in opposite phases would give a triply degenerate normal mode, while their movement in the same phases would represent a residuum of three translations.

Thus, the structure would have only nine different frequencies of vibration, while the number of normal modes would be 45 which together with the residuum of the three translations would account for the 48 degrees of freedom of movement of 8 atoms of magnesium and 8 atoms of oxygen when added together. The description of the modes of vibration corresponding to each of the nine different frequencies is entered in the second column of Table II, while their respective degeneracies are shown in the third column of the table. These degeneracies are the same as shown in Table I, but they now total up to 48 instead of to 24 as in the former table.

The modes have been shown in the first column of Table II in the order of the magnitude of their respective frequencies suggested by the approximate formulæ of the dynamical theory to be given presently. But this arrangement is subject to revision on the basis of a more accurate evaluation of those frequencies. It will be noticed that at the top of the table listed as mode I appears the triply degenerate oscillation of the Mg and O atoms in the structure moving against each other in opposition of phase. It will also be noticed that next to it in the descending order of frequency appear the tangential and normal modes of oscillation of the cubic layers of atoms. These are listed in the table as modes II and III, while two other modes of oscillation of the cubic layers in which the phases of movement of the Mg



TABLE II

Sl. No.	Description of Mode	Degeneracy
I	Oscillation of the Mg and O atoms in opposite phases ..	3
II	Tangential oscillations of the cubic planes, Mg and O atoms having opposite phases	6
III	Normal oscillations of the cubic planes, Mg and O atoms having same phases	3
IV	Normal oscillations of the octahedral planes of O atoms	4
V	Tangential oscillations of the octahedral planes of O atoms	8
VI	Normal oscillations of the octahedral planes of Mg atoms	4
VII	Tangential oscillations of the octahedral planes of Mg atoms	8
VIII	Normal oscillations of the cubic planes, Mg and O atoms having opposite phases	3
IX	Tangential oscillations of the cubic planes, Mg and O atoms having same phases .. .. .	6
X	Translations .. .. .	3
	Total degrees of freedom	48

and O atoms are different appear at the bottom of the table as VIII and IX respectively. The oscillations of the octahedral layers of atoms appear in an intermediate position as IV, V, VI and VII respectively.

#### 4. DYNAMICAL THEORY: FIRST APPROXIMATION

The normal modes of atomic vibration in a crystal remain unaltered when a unit translation is given to the structure along any one of its three axes. Accordingly, it is sufficient to write down and solve the equations of motion of the atoms contained in any one unit cell of the structure. The features of the vibration deduced therefrom would equally well describe the possible atomic movements in the other cells of the structure. In the present problem, therefore, we have only to frame the equations of motion of a magnesium atom and of an adjoining oxygen atom in the structure



for each of the possible modes of vibration deduced from the geometry of the structure. Their solution would give us the frequencies of those modes of vibration.

The forces acting on an atom which determine its movements are those arising from the displacements of other atoms in the crystal by reason of their mutual interactions. We shall proceed on the assumption that the interactions between any two atoms are determined by their *relative* displacements measured from the positions they occupy when at rest in the crystal. The forces of interaction may be expected to be greatest as between atoms which are near neighbours and to diminish rapidly in respect of those atoms which are further and further removed from each other.

The nearest neighbours of each magnesium atom in the MgO structure are six oxygen atoms. These are situated in pairs, one on either side along the  $x$ ,  $y$  and  $z$  axes of the structure. Likewise, each oxygen atom has six magnesium atoms as its nearest neighbours arranged in a similar fashion. We shall, in the first instance, proceed to work out the dynamics of the vibrations taking into account only the interactions between each magnesium atom and its six neighbouring oxygen atoms and *vice versa*. It is clear that two force-constants which we shall denote as  $\alpha$  and  $\beta$  respectively would suffice to specify these interactions. The constant  $\alpha$  refers to the interaction between an Mg atom and an O atom arising from their relative displacement *along* the direction of the cubic axis on which they both lie. The force resulting from such displacement would be parallel to the direction of the displacement. The constant  $\beta$  refers to the interaction arising from a relative displacement *transverse* to the line joining the two atoms and parallel to one of the other two cubic axes. In this case as well, the resulting force would be parallel to the direction of such displacement.

We denote by  $m_1$  and  $m_2$  the masses of the Mg and O atoms respectively.  $\xi_1, \eta_1, \zeta_1$  and  $\xi_2, \eta_2, \zeta_2$  are the displacements of the Mg and O atoms under consideration respectively along the  $x, y$  and  $z$  axes. The forces acting on these atoms are found by multiplying the displacements of the interacting atoms relatively to each of them by the appropriate force-constants and adding them up. The equations are then solved by writing

$$\xi_1 = x_1 \sin \omega t, \quad \eta_1 = y_1 \sin \omega t, \quad \text{etc.}$$

and eliminating the quantities  $x_1, y_1$ , etc., which represent amplitudes. An expression is then obtained which gives  $\omega^2$  in terms of  $\alpha, \beta$  and the masses  $m_1$  and  $m_2$ . We shall consider in turn the different modes of vibration indicated by Table I as possible for a face-centred cubic lattice,



The first case we shall consider is that in which the Mg atoms and O atoms oscillate as groups along the  $x$ -axis. The equations of motion are then

$$\begin{aligned} m_1 \frac{d^2 \xi_1}{dt^2} &= -K_0 (\xi_1 - \xi_2) \\ m_2 \frac{d^2 \xi_2}{dt^2} &= -K_0 (\xi_2 - \xi_1) \end{aligned}$$

where  $K_0$  is an abbreviation for  $(2\alpha + 4\beta)$ . Proceeding as already indicated, we obtain a quadratic equation for  $\omega_1^2$ , the solutions of which are

$$\omega_1^2 = \frac{K_0}{\mu}, \quad \omega_{10}^2 = 0 \quad (1)$$

where  $\mu$  is the reduced mass given by the formula  $1/\mu = 1/m_1 + 1/m_2$ . The first solution represents mode I in Table II above, while the zero frequency represents the translations appearing at the foot of that table.

The next case is that of the tangential oscillation of the cubic layers of atoms which are parallel to the  $yz$  plane along the  $y$ -axis. The alternate layers oscillate in opposite phases. The equations of motion are:

$$\begin{aligned} m_1 \frac{d^2 \eta_1}{dt^2} &= -K_0 \eta_1 + 2\alpha \eta_2 \\ m_2 \frac{d^2 \eta_2}{dt^2} &= 2\alpha \eta_1 - K_0 \eta_2 \end{aligned}$$

The solutions of these equations are:

$$\omega_{2,9}^2 = \frac{1}{2} \frac{K_0}{\mu} \pm \left[ \frac{K_0^2}{4\mu^2} - \frac{(K_0^2 - 4\alpha^2)}{m_1 m_2} \right]^{\frac{1}{2}} \quad (2)$$

The alternative signs appearing in formula (2) give the frequencies of vibration  $\omega_2$  and  $\omega_9$  respectively. The higher frequency  $\omega_2$  refers to the case in which the Mg and O atoms appearing in the same  $yz$  planes move in opposite phases. The lower frequency  $\omega_9$  represents the case in which the Mg and O atoms appearing in the same  $yz$  planes move in the same phase.  $\omega_2$  and  $\omega_9$  refer respectively to the modes listed as II and IX in Table II. From formula (2) it is evident that

$$\omega_9^2 = \omega_1^2 - \omega_2^2.$$

The third case we shall consider is that in which the cubic layers of atoms in the crystal lying in the  $yz$  planes oscillate normally to themselves along the  $x$  axis, the alternate layers being in opposite phases. The equations of motion are;



$$m_1 \frac{d^2 \xi_1}{dt^2} = -K_0 \xi_1 - (K_0 - 8\beta) \xi_2$$

$$m_2 \frac{d^2 \xi_2}{dt^2} = - (K_0 - 8\beta) \xi_1 - K_0 \xi_2.$$

The solutions of these equations are:

$$\omega_{3,8}^2 = \frac{\frac{1}{2} K_0}{\mu} \pm \left[ \frac{\frac{1}{4} K_0^2}{\mu^2} - \frac{32\alpha\beta}{m_1 m_2} \right]^{\frac{1}{2}}. \quad (3)$$

The alternative signs appearing in the formula give the two frequencies of vibration  $\omega_3$  and  $\omega_8$ . The higher frequency  $\omega_3$  represents the case in which the Mg and O atoms which appear in any yz plane oscillate in the same phase, while the Mg and O atoms adjacent to each other in adjoining yz layers vibrate in opposite phases. The lower frequency  $\omega_8$  refers to the case in which the Mg and O atoms which appear in the same yz planes move in opposite phases, while the Mg and O atoms which are nearest to each other in adjacent yz layers oscillate in the same phase.  $\omega_3$  and  $\omega_8$  refer respectively to the modes listed as III and VIII respectively in Table II. From the formula (3), it is evident that

$$\omega_8^2 = \omega_1^2 - \omega_3^2.$$

We have next to consider the oscillations of the octahedral layers of atoms normally or tangentially to themselves. The Mg and O atoms are located in separate octahedral layers which alternate and are equidistant from each other. Hence, when two layers of Mg atoms oscillate in opposite phases, the layer of oxygen atoms midway between them remains at rest, and *vice versa*. A single equation of motion determines the frequency of oscillation for the magnesium atoms, while another such equation yields the frequency for the oxygen atoms. It is also evident that when the interactions only with the nearest neighbours are considered, the frequency for oscillations normal and tangential to the octahedral planes would not be different. We obtain

$$\omega_{4,5}^2 = \frac{K_0}{m_2} \quad (4)$$

for the modes listed as IV and V in Table II and

$$\omega_{6,7}^2 = \frac{K_0}{m_1} \quad (5)$$

for the modes listed as VI and VII in Table II,



## 5. DYNAMICAL THEORY: SECOND APPROXIMATION

In the foregoing, we took into account only the interactions between the atoms which are nearest to each other. This enables a first approximation to be obtained in a simple manner for the frequencies of vibration and permits of their being arranged, at least provisionally, in an ordered sequence. There is no difficulty, however, in taking the interactions with more distant neighbours into account and finding more exact formulæ. Besides the six neighbouring oxygen atoms, each magnesium atom has twelve magnesium atoms as next nearest neighbours located on the face-diagonals. It has also eight oxygen atoms as more distant neighbours located on the body-diagonals. Likewise, each oxygen atom has twelve oxygen atoms as next nearest neighbours and eight magnesium atoms as more distant neighbours. The movements of these neighbours relatively to the atom under consideration and the interactions arising therefrom have to be taken into consideration, in framing its equations of motion and deducing therefrom the frequencies of its vibration. We shall consider in succession the various modes of vibration listed in Table II.

*Mode I.*—In addition to the force-constants  $\alpha$  and  $\beta$  already introduced, we have to consider a third force-constant  $\gamma$ , which expresses the interactions between the magnesium atoms and the oxygen atoms located along the body-diagonals of the cubic structure. It is readily shown that the frequencies are given by

$$\omega_1^2 = \frac{K}{\mu} \quad \text{or} \quad \omega_{10} = 0 \quad (6)$$

where  $K$  is an abbreviation for  $(2\alpha + 4\beta + 8\gamma)$ .

*Modes II and IX.*—In these modes, we have now to consider also the interactions of each Mg atom with the twelve Mg atoms in its neighbourhood. Likewise, we have to take into account the interaction of each O atom with its twelve neighbouring O atoms. The forces and displacements with which we are concerned in these interactions are parallel to each other and to one or another of the three cubic axes. Four of the atoms are located in each of the three cubic planes containing the atom under consideration. It emerges that in four cases out of the twelve, the force and the displacement are both perpendicular to the cubic plane in which the interacting atoms are situated, while in the remaining eight cases, they are both parallel to that plane. We have accordingly to introduce two new force-constants  $\theta_1$  and  $\phi_1$  for the interactions between the magnesium atoms, and likewise



two other force-constants  $\theta_2$  and  $\phi_2$  for the interactions between the oxygen atoms. The equations of motion then take the form

$$m_1 \frac{d^2 \eta_1}{dt^2} = - (K + 8\theta_1 + 8\phi_1) \eta_1 + (K - 4\beta - 16\gamma) \eta_2$$

$$m_2 \frac{d^2 \eta_2}{dt^2} = (K - 4\beta - 16\gamma) \eta_1 - (K + 8\theta_2 + 8\phi_2) \eta_2.$$

Substituting

$$\eta_1 = y_1 \sin \omega t \quad \text{and} \quad \eta_2 = y_2 \sin \omega t$$

and eliminating  $y_1$  and  $y_2$ , we obtain a quadratic equation which enables  $\omega_{2,9}^2$  to be expressed in terms of the force-constants and the masses  $m_1$  and  $m_2$ .

*Modes III and VIII.*—Only five out of the seven force-constants already introduced appear in the equations of these two modes.

$$m_1 \frac{d^2 \xi_1}{dt^2} = - (K + 16\phi_1) \xi_1 - (K - 8\beta) \xi_2$$

$$m_2 \frac{d^2 \xi_2}{dt^2} = (K - 8\beta) \xi_1 - (K + 16\phi_2) \xi_2.$$

Substituting

$$\xi_1 = x_1 \sin \omega t \quad \text{and} \quad \xi_2 = x_2 \sin \omega t$$

and eliminating  $x_1$  and  $x_2$ , we obtain a quadratic equation which gives  $\omega_{3,8}^2$  in terms of the force-constants and the masses  $m_1$  and  $m_2$ .

*Modes IV, V, VI and VII.*—We have now to introduce two additional force-constants  $\psi_1$  and  $\psi_2$ , which represent interactions in which the force and the displacement are mutually perpendicular, the displacement being along one cubic axis and the force along another cubic axis, while the interacting atoms lie in the plane defined by the two axes.  $\psi_1$  refers to the case in which the interacting atoms are both of magnesium, while  $\psi_2$  refers to the case in which they are both oxygen atoms. These force-constants appear in considering the movements of the octahedral layers either normally or tangentially to themselves, by reason of the simultaneous movements along all the three cubic axes or along two cubic axes which need to be taken into account of in these cases. The equations of motion for normal and tangential movements of a magnesium atom respectively are;



$$m_1 \frac{d^2 \xi_1}{dt^2} = - (K + 4\theta_1 + 8\phi_1 + 8\psi_1) \xi_1$$

$$m_1 \frac{d^2 \xi_1}{dt^2} = - (K + 4\theta_1 + 8\phi_1 - 4\psi_1) \xi_1.$$

The frequencies are therefore respectively:

$$\omega_6^2 = \frac{(K + 4\theta_1 + 8\phi_1 + 8\psi_1)}{m_1}$$

$$\omega_7^2 = \frac{(K + 4\theta_1 + 8\phi_1 - 4\psi_1)}{m_1}. \quad (7)$$

The equations of motion for normal and tangential oscillations of an oxygen atom are respectively

$$m_2 \frac{d^2 \xi_2}{dt^2} = - (K + 4\theta_2 + 8\phi_2 + 8\psi_2) \xi_2$$

$$m_2 \frac{d^2 \xi_2}{dt^2} = - (K + 4\theta_2 + 8\phi_2 - 4\psi_2) \xi_2.$$

The frequencies are therefore respectively

$$\omega_4^2 = \frac{(K + 4\theta_2 + 8\phi_2 + 8\psi_2)}{m_2}$$

$$\omega_5^2 = \frac{(K + 4\theta_2 + 8\phi_2 - 4\psi_2)}{m_2}. \quad (8)$$

## 6. SUMMARY

The fundamental property of a normal vibration indicated by the classical dynamics, *viz.*, that the particles in the system oscillate with the same frequency and in the same or opposite phases, considered in relation to the three-dimensionally periodic structure of a crystal enables the possible modes of atomic vibration in a crystal to be uniquely characterised and enumerated. The simplicity and high symmetry of the structure of MgO enables this procedure to be carried further and the modes of normal vibration to be completely described and explicit formulæ obtained from their frequencies. It emerges that the structure of MgO has nine distinct frequencies of vibration. Expressions have been derived for these frequencies of these modes, both in the first and in the second approximation,



# THE VIBRATIONS OF THE $\text{MgO}$ CRYSTAL STRUCTURE AND ITS INFRA-RED ABSORPTION SPECTRUM

## Part III. Comparison of Theory and Experiment

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### 1. INTRODUCTION

PART I of this memoir dealt with the observed infra-red behaviour of  $\text{MgO}$  over the spectral range covered by the instruments at the disposal of the author. In Part II, the normal modes of vibration of the atomic nuclei in the crystal about their positions of equilibrium were deduced from the principles of classical mechanics and expressions were given for the frequencies of the nine modes which were shown to be possible. In the present part, we shall concern ourselves with a comparison of the results of experiment and the consequences of the theory. Such a comparison has necessarily to be based on the nature of the relationship between infra-red activity and the modes of vibration of the atomic nuclei. We shall freely make use of the ideas and principles which have emerged from studies on the infra-red behaviour of diatomic, triatomic and polyatomic molecules, as also of crystals having more complex structures. It will be found that these ideas and principles when applied to the particular circumstances of the case enable a highly satisfactory concordance to be established between the facts of experiment recorded in Part I of the memoir and the dynamical theory developed in Part II.

### 2. INFRA-RED ACTIVITY OF THE FIRST ORDER

A fact which emerges very clearly from the experimental studies described in Part I is that the normal mode which is strongly active as a fundamental has also the highest frequency of all the active normal modes. The theoretical formulæ for the frequencies obtained and set out in Part II also show that the mode of vibration in which the  $\text{Mg}$  and the  $\text{O}$  atoms oscillate in opposite phases and in which the oscillation repeats itself from cell to cell without change of phase has a higher frequency than all the other eight



modes. This is obvious from the approximate formulæ given in Section 4 of Part II and the situation is not altered when the higher approximations set out in Section 5 are considered. It is further evident that this normal mode would exhibit a powerful infra-red activity of the first order. For, the displacements of electric charge resulting from the approach to or recession from each other of the two dissimilar atoms Mg and O would occur in the same phase in the successive cells of the structure and hence their effects would be cumulative.

Considering now the eight other normal modes, they can all be described as movements of the Mg atoms or of the O atoms alone or of both sets of atoms together in one or another of the different directions permitted by the symmetry of the structure. But a common feature of all the eight modes is that these movements alternate in phase along one or two or all three of the directions which are the edges of the unit rhombohedral cell of the lattice. Hence, the displacements of charge in the successive cells of the structure are in alternate phases. Therefore, when summed up over an element of volume including a block of eight contiguous cells in the structure, the displacements of charge would cancel out. It follows that all the eight modes under reference would fail to exhibit any infra-red activity of the first order. In other words, we cannot expect their fundamental frequencies to manifest themselves as absorption maxima in the spectrographic records. This again is in agreement with what is actually observed.

Here a distinction must be drawn between the four normal modes which involve simultaneous movements of the Mg and O atoms in directions which are either normal or tangential to the cubic planes of the crystal and the four other normal modes in which the Mg atoms alone or the O atoms alone oscillate in directions which are normal or tangential to the octahedral planes of the crystal. As has already been remarked in Part II, the Mg atoms and the O atoms appear in distinct layers in the octahedral planes in such manner that each Mg layer has O layers on either side of it at the same distance and each O layer has likewise Mg layers situated symmetrically on either side. Further, in the normal modes of these four species, the Mg layers on either sides of the O layers, or the O layers on either side of the Mg layer oscillate in opposite phases. As a consequence, the displacements of electric charge on either side of the middle layer are in opposite directions. When summed up over the volume element containing eight unit cells of the structure, they cancel out. Such cancellation is clearly *absolute*, in other words, it is not limited to the case in which the movements of charge are regarded as of very small amplitude and therefore strictly harmonic in character.



Thus, the two categories of normal modes, viz., those in which the Mg and O atoms oscillate simultaneously and those in which they oscillate separately stand on a different footing. The former are inactive in the first-order absorption by reason of the alternation of phase in the successive cells of the structure. The absence of activity depends on the oscillation of being of small amplitude and the displacements of charge resulting therefrom being of equal magnitude but opposite in phase in successive cells. On the other hand, in the second category, the cancellation is effective irrespective of the actual amplitude of the oscillations.

### 3. INFRA-RED ACTIVITY OF HIGHER ORDERS

The considerations set forth above naturally lead us to consider the possibility of the normal modes exhibiting infra-red activity of higher orders, in other words of manifesting themselves in the absorption spectra as overtones of the fundamentals. The appearance of overtones in the infra-red absorption spectra of diatomic and polyatomic molecules is a familiar fact of experience. It is also well known that they are much weaker than the fundamentals which is indicated by the fact that their observation needs the use of much thicker absorbing layers. The explanation for their appearance usually given is based on the hypothesis of the anharmonicity of the molecular vibrations of which the effect comes into prominence when the oscillations of the atomic nuclei are of very large amplitude. In these circumstances, the periodic displacements of electric charge which give rise to the absorption of infra-red radiation include components not only of the fundamental frequencies but also the overtones of those frequencies. Absorption of the energy of radiations having the overtone frequencies and its transformation to the energy of nuclear vibrations is thereby made possible.

The important point regarding the infra-red activity of higher orders is that the amplitudes of nuclear vibration should be large. Even when this condition is satisfied, considerations regarding the symmetry of the modes of vibration may, in particular cases, totally exclude the manifestation of the effect of the periodic displacements of charge and hence also the possibility of the infra-red activity of all orders. We have already noticed such a situation in the case of the modes involving oscillation of the Mg atoms alone or of the O atoms alone in directions normal or tangential to the octahedral layers. Hence these four modes could not be expected to manifest themselves as overtones in the infra-red absorption spectra. The position is different in regard to the five other modes which involve simultaneous movements of the Mg and the O atoms. No such restriction based



on considerations of the symmetry appears in their cases. Hence we may expect overtones of all these five modes to manifest themselves in the absorption spectra, provided the necessary condition of the largeness of the amplitudes of the nuclear vibrations is satisfied.

The dynamical theory set out in Part II of the memoir is based on the well-known theorem in classical mechanics regarding the small vibrations of a connected system of particles about their positions of equilibrium. The theorem enables the relative magnitudes of the amplitudes of their vibration in any particular normal mode to be evaluated. But it leaves their absolute magnitudes undetermined. But, since we are now concerned with the absorption of radiation, the introduction of the ideas of the quantum theory which is inevitable results in making the amplitudes of vibration fully determinate. The incident radiation consists of energy quanta of magnitude  $h\nu$ . Assuming for the sake of simplicity that the oscillators are strictly harmonic with a frequency  $\nu_0$ , their energy would go up with increasing amplitude by successive equal steps of  $h\nu_0$ . The successive orders of absorption would then appear as a consequence of equating  $h\nu$  to  $h\nu_0$ , or  $2h\nu_0$  or  $3h\nu_0$  or  $4h\nu_0$ . Mechanical anharmonicity of the oscillators would only result in the energy values deviating from this regular harmonic sequence. What is needed for the possibility of infra-red activity of higher orders is that the oscillations of electric charge associated with the nuclear movements should include a harmonic series of components having the frequencies  $2\nu_0$ ,  $3\nu_0$ ,  $4\nu_0$ , etc. The energy of radiation having those frequencies can then be taken up by the moving charges and transferred to the atomic nuclei as energy of mechanical movement, in other words, as heat energy.

From what has been stated, it is clear that if we identify the mechanical oscillators in the crystal as *domains of macroscopic size*, infra-red absorptions of orders higher than the first would be impossible. For, when the oscillatory energy of such a domain is quantised, the actual amplitudes of oscillation of the atomic nuclei and therefore also the movements of electric charge associated with them would be infinitesimal. The only possibility would then be the absorption of the first order in which  $h\nu = h\nu_0$  and absorptions of higher order cannot arise. Thus, for absorptions of higher order to be at all possible, we must assume the oscillators in the crystal to be of extremely small dimensions, in other words to be the unit cells of the crystal structure or small groups of such unit cells. The oscillators whose normal modes were listed and enumerated in Part II of the memoir were twice as large in each direction as the unit cells of the crystal structure. If their energies are quantised, the amplitude of the atomic oscillations in



domains of such small size would be sufficiently large to permit of infra-red absorption of higher orders than the first.

We may sum up the results of this discussion by the statement that of the nine normal modes listed in Table II of Part II of the memoir, Mode I would be active both as a fundamental and as overtones, Modes II, III, VIII and IX would be inactive as fundamentals but could be active as overtones, while Modes IV, V, VI and VII would not be active either as fundamentals or as overtones.

#### 4. FREQUENCIES OF THE ACTIVE MODES

The frequencies of the normal modes of vibration were derived in Section 4 of Part II on the assumption that the only interactions which need be taken into account are those between unlike atoms in the structure. This assumption is valid only in respect of the active mode of the highest frequency. The approximate formulæ derived on that basis are however useful as they enable the frequencies of the five active modes to be expressed in terms of each other. Two force-constants appear in the formulæ, viz.,  $\alpha$  and  $\beta$ ,  $\alpha$  being the longitudinal and  $\beta$  the transverse component of the interaction between adjacent unlike atoms. It may be presumed that  $\alpha$  is greater than  $\beta$ , but the ratio of  $\alpha$  to  $\beta$  is not known. We assume the highest frequency of the five to be  $490 \text{ cm.}^{-1}$  and compute the others for various values of the ratio  $\alpha/\beta$ , viz.,  $\alpha = \beta$ ,  $\alpha = 2\beta$  and  $\alpha = 3\beta$ .

Table I below shows the results thus obtained.

TABLE I

*Frequencies of the normal modes: Observed and calculated ( $\text{cm.}^{-1}$ )*

	Mode I	Mode II	Mode III	Mode VIII	Mode IX
Observed ..	490	423	365	313	277
Calculated .. $\alpha = 2\beta$	490	428	380	309	237
Calculated .. $\alpha = 3\beta$	490	441	393	293	212
Calculated .. $\alpha = \beta$	490	408	408	271	270



It will be seen that the five frequencies follow each other in the same order for all three  $\alpha/\beta$  ratios, though the actual magnitudes of the calculated frequencies are different. The best agreement between the calculated and the spectroscopically determined frequencies results from the most reasonable assumption for the  $\alpha/\beta$  ratio, viz., that  $\alpha = 2\beta$ . The mode of lowest frequency, viz., Mode IX is however seen to be an exception. Mode IX, it may be remarked here, is an oscillation of the cubic planes tangential to themselves, the Mg and the O atoms in those planes moving in the same phase. Like all the other modes listed in Table I except the first, it is inactive as a fundamental but active as a octave. By the nature of the case, however, such activity would be feeble. Referring to the absorption curves of the thinnest MgO film reproduced as the upper of the two records in Fig. 10 of Part I of this memoir, it will be noticed that the transmission falls off more steeply in the region of wavelengths greater than  $20\mu$  than towards shorter wavelengths. The form of the graph between  $16\mu$  and  $20\mu$  indicates that a specific absorption is operative which is located midway between them, viz., at about  $18\mu$ . We are, therefore, justified in adding  $277\text{ cm.}^{-1}$  and the wavelength  $36\mu$  to the list of normal modes and their characteristic wavelengths in the summary of experimental results which concludes Part I.

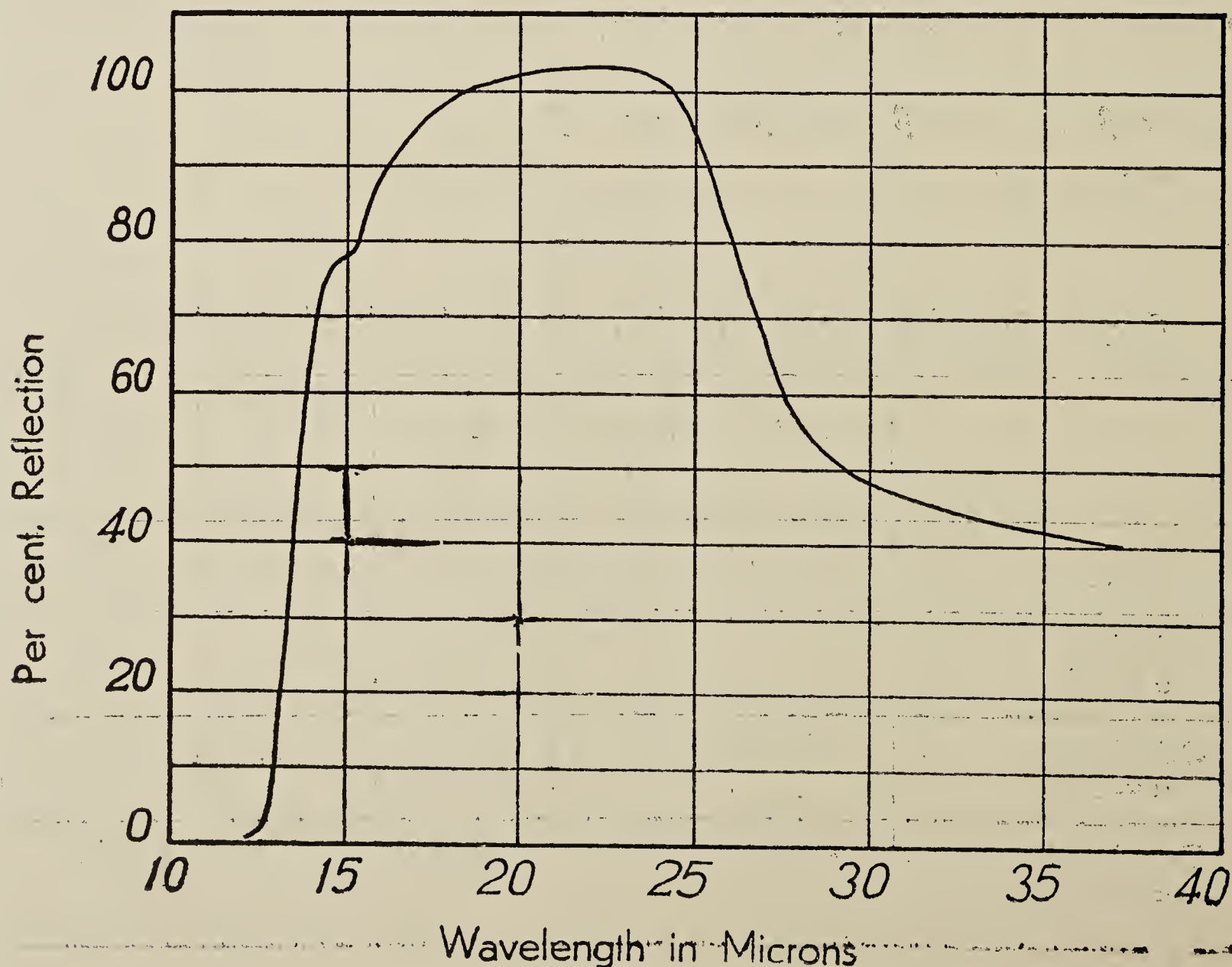


FIG. 1. Reflecting power of MgO surface.



## 5. RELATION BETWEEN REFLECTIVITY AND INFRA-RED ABSORPTION

We may now proceed to discuss the manner in which the reflecting power of the surface of an MgO crystal changes with wavelength in the spectral range between  $13\mu$  and  $36\mu$ . The experimental results obtained and reported by Burstein, Oberly and Plyler (1948) have already been referred to in Part I of this memoir. Their figure which shows the reflecting power as compared with an aluminium mirror is reproduced as Fig. 1 above in the text. One might expect that the peak of the reflecting power would appear at the wavelength  $20.40\mu$  which corresponds to the active fundamental frequency of  $490\text{ cm.}^{-1}$ . However, we have also to consider in this connection, the other normal modes of vibration of the crystal. Besides the active fundamental at  $20.40\mu$ , there is the inactive fundamental close to it in frequency which has a characteristic wavelength at  $23.64\mu$  and a series of other inactive fundamentals at still greater wavelengths, viz.,  $27.4\mu$ ,  $32\mu$  and  $36\mu$ . Then again, in the region of wavelengths less than  $20.40\mu$ , octaves of the normal modes appear which have their characteristic wavelengths at  $10.20\mu$ ,  $11.82\mu$ ,  $13.7\mu$ ,  $16\mu$  and  $18\mu$  respectively. All these octaves have been shown to be active in absorption. The possibility therefore arises of their making an observable contribution to the reflecting power of an MgO surface.

As already noticed, the absorptions located at  $10.20\mu$  and  $11.82\mu$  are so weak that they can only be recorded with comparatively thick plates. We may, therefore, exclude them from consideration and need only take note of the absorptions located at  $13.7\mu$ , at  $16\mu$  and  $18\mu$ . It is significant that the reflective power of MgO reaches large values in this range of wavelengths. It rises very steeply at about  $13.7\mu$  and after exhibiting an inflexion or arrest at  $15\mu$ , goes up again in the wavelength range between  $16\mu$  and  $18\mu$  before it reaches the peak reflectivity beyond  $20\mu$ . Indeed, the course of the reflectivity curve is itself the clearest demonstration that the octaves at  $13.7\mu$ ,  $16\mu$  and  $18\mu$  contribute notably to the reflecting power; the arrest at  $15\mu$  arises from the frequency gap between the first two.

Figure 1 shows that the reflecting power continues to increase a little beyond  $20.40\mu$  and is greatest at about  $24\mu$ . Beyond  $24\mu$ , it falls rather quickly at first and then more slowly, but remains large up to  $35\mu$  and beyond. These facts find a natural explanation if we assume that the second fundamental having its characteristic wavelength at  $23.64\mu$  makes a notable contribution to the reflecting power. This is indeed to be expected. For, when the frequency of the radiation is equal to or near the frequency of the active fundamental, the movements of electric charge at and near the surface



of the crystal would be large. In these circumstances, the different normal modes of vibration may be expected to influence each other in such a manner that a mode which is ordinarily inactive could be excited to activity. That the observed powerful reflection extends up to  $24\mu$  and even beyond it is therefore not surprising.

## 6. FREQUENCIES OF THE INACTIVE MODES

The approximate formulæ given in Section 4 of Part II enable us also to evaluate the frequencies of the inactive modes, *viz.*, those in which the O atoms alone or the Mg atoms alone oscillate in terms of the highest active frequency, *viz.*,  $490\text{ cm.}^{-1}$ . We obtain  $380\text{ cm.}^{-1}$  and  $309\text{ cm.}^{-1}$  respectively as the frequencies of vibration of the O and of the Mg atoms. It is evident, however, that these figures are an underestimate of the actual frequencies of these modes. For, as is also clear from the formulæ of Section 5 of Part II, the frequencies of these modes are determined by the interaction of each oscillating atom with six like atoms in its immediate vicinity as well as with the six unlike atoms which are its nearest neighbours. As the distance between like atoms is only  $\sqrt{2}$  times the distance between unlike atoms, we may safely assume that the two sets of interactions would be of comparable magnitudes and hence that the vibration frequencies would be definitely greater than  $380\text{ cm.}^{-1}$  and  $309\text{ cm.}^{-1}$  indicated by the first approximation.

The neglect of the interactions between like atoms also results in the frequencies of oscillations of the Mg and of the O atoms normal to the octahedral planes having the same frequency as oscillations tangential to them. Actually, however, oscillations normal to the octahedral planes may be expected to have frequencies noticeably greater than the modes tangential to those planes.

Earlier, it was remarked that by reason of their geometric symmetry, Modes IV, V, VI and VII would be totally inactive, in other words, that they would be wholly inaccessible to observation by the methods of infra-red spectroscopy. This statement was, however, based on the assumption that the normal vibrations of the structure are completely independent of each other. Since, however, we are concerned with the infra-red activity of higher orders than the first, the amplitudes of vibrations involved are not small and the normal modes cannot therefore be completely independent of each other. The possibility thus arises of the inactive modes or rather of their overtones revealing themselves in the spectroscopic records by a



species of induced activity resulting from the contiguity of their frequencies to the frequencies of strongly active modes.

Referring to the spectrographic records reproduced as Figs. 3, 4, 5, 6, 7 and 8 in Part I of this memoir, it will be noticed that the transmission curve in the region between  $10.20\mu$  and  $11.82\mu$  exhibits certain curious features appearing in all of them and at precisely the same spectral wavelengths. The transmission which is a minimum at  $10.20\mu$  rises to a maximum and then drops to the second minimum at  $11.82\mu$ ; but between the two minima, the graph does not follow a smooth curve but bends inwards more or less sharply in the vicinity of two wavelengths, one on either side of the  $11\mu$  ordinate. One such bend may be located at  $10.8\mu$  and the other at  $11.2\mu$ . The sharp bends at these two positions appear very clearly, for example, in Fig. 6 of Part I. The frequencies in wave-numbers at which these singularities appear are respectively  $925\text{ cm.}^{-1}$  and  $893\text{ cm.}^{-1}$ . If we assume that they represent the octaves of two normal modes exhibiting induced activity, their frequencies would be  $463\text{ cm.}^{-1}$  and  $446\text{ cm.}^{-1}$ , substantially greater than the  $380\text{ cm.}^{-1}$  indicated by the rough calculation in which the interactions between the oxygen atoms nearest to each other are totally ignored. But the increases are not greater than what might be expected to result from such interactions being taken into account.

The induced activity of Modes VI and VII in which the magnesium atoms alone oscillate is not so conspicuously exhibited in the spectrograms reproduced in Part I of this memoir. Indications of them, however, appear in the wavelength range between  $12\mu$  and  $13\mu$  in Figs. 6, 7 and 8 of Part I. The sharp bends in the transmission curve at  $12.5\mu$  and at  $12.9\mu$  noticed in Fig. 8 are perhaps their clearest manifestation. Interpreting these singularities as arising from the octaves of the normal Modes VI and VII, we obtain their characteristic wavelengths at  $25\mu$  and  $25.8\mu$  respectively and their characteristic frequencies as  $400\text{ cm.}^{-1}$  and  $387\text{ cm.}^{-1}$ . These are substantially higher than the rough value of  $309\text{ cm.}^{-1}$  which results when we neglect the interactions between each magnesium atom and the six nearest magnesium atoms which appear in the more exact expressions for the frequencies of these modes. The observed frequencies indicate that these interactions are far from being weak or negligible. The electron atmospheres of the magnesium atoms extend further from their nuclei and hence would come into closer contact with each other in the unit cells of the structure than would be the case for the oxygen atoms. Hence the forces of interaction as between like atoms may be expected to be even more powerful for Mg than for O atoms.



## 7. SOME CONCLUDING REMARKS

Our purpose so far has been to show how closely the consequences of the dynamical theory set out in Part II and the observed infra-red behaviour of MgO in absorption and in reflection described in Part I fit into each other and how we are thereby enabled to obtain a clear and comprehensive view of the subject. Formal considerations based on the concept of interatomic forces, of displacements of electric charge resulting from atomic movements and of their symmetry characters were sufficient for that purpose. It would not, however, be superfluous to add a few remarks here regarding other fundamental aspects of the infra-red behaviour of crystals.

A question of some importance is the role played respectively by the atomic nuclei and by the electrons in the infra-red activity of crystals. The displacements of the massive atomic nuclei from their positions of equilibrium are necessarily involved, since the frequency of the absorbed radiation is identical with or approximates to a frequency of vibration of the atomic nuclei about their positions of equilibrium or to a small multiple thereof. But we have also to emphasise the part played by the electrons which hold the nuclei together and determine the magnitude of the interatomic forces and hence also effectively determine the frequencies of the nuclear vibrations. There can be little doubt that it is the displacement of these electrons induced by the field of the incident radiation which is the effective cause of infra-red absorption. The nuclear movements can make no direct contribution of importance to the displacements of electric charge. For, the oscillations of some of the atomic nuclei are in opposition of phase to the oscillations of the others and hence their effects would cancel out.

It follows from what has been stated above that the dynamic theory of the vibrations of the atomic nuclei and its consequences represent only one aspect of the subject of the infra-red behaviour of crystals. The other aspect is the behaviour of the electrons which hold the nuclei together in their places. These two aspects are closely related to each other. Hence, while there should be an easily observable correlation between the features of the vibration spectra of the atomic nuclei deduced from the theory and the spectral characters of the absorption and reflection of infra-red radiation as found in experiment, a complete agreement in respect of all details of their features is scarcely to be expected.

## 8. SUMMARY

The description of the nine normal modes of vibration and their frequency formulæ given in Part II enable them to be grouped together in



respect of infra-red activity and arranged in each group in diminishing order of frequency. A detailed comparison then becomes possible between the consequences of the theory and the experimental results set out in Part I. A comprehensive and satisfactory agreement emerges from the comparison. The modes can be identified and their frequencies determined directly from the spectroscopic records. The manner in which the reflectivity of an MgO surface varies with the wavelength of the infra-red radiation also receives a satisfactory elucidation.



# THE VIBRATIONS OF THE MgO CRYSTAL STRUCTURE AND ITS INFRA-RED ABSORPTION SPECTRUM

## Part IV. Evaluation of Its Specific Heat

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### 1. INTRODUCTION

EINSTEIN's classic paper of 1907 introducing his theory of specific heats was based on an application of the fundamental notions of the quantum theory and of thermodynamics to the problem of determining the thermal behaviour of a body assumed to be constituted of a great number of structural elements, each of which is an oscillator having a definite frequency of vibration. Basing himself on the assumption that their energy of vibration obeys the quantum rules, Einstein obtained an expression for the total vibrational energy of the body, in other words for its heat content, in terms of the frequency or frequencies of vibration of the oscillators, their numbers and the absolute temperature. Einstein's theory and its results may be summed up by the statement that the thermal energy content of a substance is determined by the vibration spectrum of the elementary structures of which it is constituted.

A well-known theorem in classical mechanics states that the small vibrations of a system of particles result from the superposition of a set of normal modes, in each of which the particles of the system vibrate with the same frequency and in the same or opposite phases, the total number of normal modes being the same as the number of degrees of dynamic freedom of the system. The normal modes in the sense of this theorem which the structure of a crystal can exhibit may be readily deduced. The argument is the same as that used earlier in Part II of this memoir for the particular case of the MgO structure. If each unit cell of the crystal contains  $p$  atoms, the crystal has  $(24p - 3)$  species of normal modes; this number is the same as the degrees of dynamic freedom of the group of  $8p$  atoms included in a volume element of which the dimensions are twice as large as those of



the unit cell; the three omitted modes are the translatory movements of the group.

In the earlier parts of this memoir it has been shown that the 45 species of normal modes indicated by the general theory for MgO ( $p = 2$ ) reduce to nine only by reason of the cubic symmetry of the crystal. These nine modes were described and their activity in the absorption and reflection of infra-red radiation was discussed. It emerged that the theory accounts in a highly satisfactory and comprehensive fashion for the observed spectroscopic properties of MgO.

TABLE I  
*Normal modes and frequencies*

Description of the mode	De- gene- racy	Frequency in cm. <sup>-1</sup>
Oscillation of the Mg and O atoms in the unit cells in opposite phases	3	490 obs.
Normal oscillation of the O atoms in the octahedral planes	4	463 obs.
Tangential oscillation of the O atoms in the octahedral planes	8	446 obs.
Tangential oscillation of the Mg and O atoms in the cubic planes in opposite phases	6	423 obs.
Normal oscillation of the Mg atoms in the octahedral planes	4	400 obs.
Tangential oscillation of the Mg atoms in the octahedral planes	8	387 obs.
Normal oscillation of the Mg and O atoms in the cubic planes in the same phase	3	365 obs.
Normal oscillation of the Mg and O atoms in the cubic planes in opposite phases	3	313 obs.
Tangential oscillation of the Mg and O atoms in the cubic planes in the same phase	6	277 obs.
Continuous spectrum	3	277 → 0

We shall now proceed to show that the thermal energy content of the MgO crystal and its variation with temperature can be fully worked out on



the basis of the same theory as its spectroscopic behaviour. We shall make use of the original ideas of Einstein and the spectroscopic data derived from our experimental studies. The specific heat of MgO and its variation with temperature thus deduced are found to be in complete agreement with the experimental data reported in the literature. It is significant that no use whatever is made of data regarding any other properties of MgO in this connection. The power and validity of the present approach to specific heat theory are thus demonstrated.

## 2. THE VIBRATIONAL SPECTRUM OF MgO

Table I given above is self-explanatory. It assembles the relevant particulars set out and discussed in the preceding parts of the memoir. The total of the degeneracies listed in the second column of the table is 48, which is also the number of degrees of dynamic freedom of a group of 8 O atoms and 8 Mg atoms which forms the dynamic unit in the crystal structure. The number of such groups is one-eighth of the number of MgO "molecules" present in the crystal. This 16-atom group is the oscillator with which we are concerned in specific heat theory. 45 out of its 48 degrees of freedom are manifested as the discrete frequencies listed in the third column of the table. The remaining 3 degrees of freedom are the translations of the oscillator. They appear as the last entry of the table and are there described as a continuous spectrum with a degeneracy three and ranging in frequency from  $277\text{ cm.}^{-1}$  down to zero. The justification for these entries will appear later.

To determine the contributions to the molecular heat of the modes with discrete frequencies shown in the third column of Table I, we use the available tabulations of the Einstein specific heat function and find its value for the particular frequency at the particular temperature under consideration. *Twice the value of the Einstein function multiplied by the degeneracy of the mode and divided by 48 gives the contribution of the mode to the molecular heat of MgO.* Proceeding in this fashion for all the nine frequencies we can sum up the results obtained. Dividing the total obtained by 40.32 which is the molecular weight of MgO, we obtain a tabulation of the specific heat of MgO as a function of the temperature, in so far as it arises from the spectrum of vibrations with discrete frequencies.

In the general case of a crystal containing  $p$  atoms in each unit cell, the  $(24p - 3)$  normal modes of vibration account for all the degrees of freedom of movement of the group of  $8p$  atoms which is the oscillator in



specific heat theory except for the three degrees which represent its translations. Even in the case of the crystals with the simplest structure ( $p = 1$ ) these translations take up only three out of every twenty-four degrees of freedom. When  $p = 2$ , as in the case of MgO, the translations represent only three out of forty-eight degrees of freedom. In the case of more complex crystals they form even a smaller proportion of the whole. Nevertheless, the movements within the crystal which they represent and the contributions which these make to the thermal energy cannot be ignored. We shall now proceed to consider these matters.

### 3. THE RESIDUAL SPECTRUM

The translations of an atomic group within a crystal would necessarily tend to displace neighbouring atomic groups and hence would set up forces resisting the movement. We are therefore led to conclude that the degrees of freedom which do not appear as internal vibrations of our dynamic units would manifest themselves as internal vibrations in elementary volumes of larger dimensions. The larger such an element of volume is, the lower would be the limit of its possible frequencies of vibration. Hence, the translations of our atomic groups would be associated with vibrational movements in the crystal whose frequencies extend from the upper limit set by the frequencies of their internal vibration down to very low values. In other words, the vibration spectrum of MgO with its discrete set of frequencies would be supplemented by a residual spectrum which is continuous and extends down to zero frequency.

We have now to determine how the modes of vibration referred to above are distributed with respect to frequency in the residual spectrum. Low frequencies arise from internal vibrations in volume elements of large size. The number of such elements included within the crystal diminishes rapidly with increase of their linear dimensions. It follows that the density of the vibrational modes in the residual spectrum would fall off quickly as their frequency diminishes.

Consider two sets of volume elements whose linear dimensions are respectively  $m$  and  $n$  times greater than those of the atomic groups which we have recognised as the dynamic units of crystal structure. The number of such volume elements would be respectively  $1/m^3$  and  $1/n^3$  times smaller than the number  $N$  in the crystal of atomic groups referred to. Let  $\nu_m$  and  $\nu_n$  be respectively the lowest frequencies of internal vibration of these volume elements. We may reasonably assume that the vibration frequencies are inversely proportional to the linear dimensions of the oscillators. We may



accordingly write  $\nu_m = f/m$  and  $\nu_n = f/n$ , where  $f$  is a constant having the dimensions of a frequency. In the limit when  $m$  approaches  $n$ , we may write  $\nu_m - \nu_n = d\nu$ . The number of oscillators whose frequencies lie within the range  $d\nu$  would be thrice the difference in the number of volume elements whose lowest frequencies are respectively  $\nu_m$  and  $\nu_n$ , and is thus the same as  $3N(1/m^3 - 1/n^3)$  in the limit where  $m$  approaches  $n$ . We may write this difference as  $9N\nu^2 d\nu/f^3$ . Integrating it over the whole frequency range covered by the residual spectrum, we should regain the number  $3N$ . We are thereby enabled to identify the constant  $f$  with the upper frequency limit  $\nu_L$  of the residual spectrum. The vibrational modes are thus distributed in the residual spectrum in the manner defined by the function  $9N\nu^2 d\nu/\nu_L^3$ .

Thus, to find the contribution to the thermal energy of the crystal arising from the residual spectrum of vibrations, we multiply the average energy of an oscillator of frequency  $\nu$  as given by Einstein's theory by the number of such oscillators distributed over its range of frequency as deduced above and integrate the product between the limits  $\nu_L$  and zero. The contribution to the specific heat would then be the differential of the energy thus evaluated with respect to temperature. The functions which come up for computation in this procedure are well known and as tabulations of them are available, it is a simple matter to find the contributions to the specific heat of MgO arising from the residual spectrum at various temperatures. These are then added to the contributions of the Einstein terms arising from the nine discrete frequencies of the lattice at the respective temperatures. The upper limit  $\nu_L$  of the frequency range covered by the residual spectrum in this evaluation is necessarily the lowest of the nine discrete frequencies of MgO, viz.,  $277 \text{ cm.}^{-1}$ . The contribution of the residual spectrum to the specific heat at different temperatures evaluated in this manner has been entered in Tables II, III and IV below as the last entry 3D (277) after the contribution of the discrete frequencies. The latter are determined from the respective Einstein functions and are indicated in these tables as 3E (490), 4E (463), etc., etc.

#### 4. COMPARISON WITH THE MEASURED SPECIFIC HEATS

The specific heat of MgO has been the subject of experimental determination by several investigators over different ranges of temperatures. Their data have been collected and put together in the form of a table at convenient intervals of temperature in the *International Critical Tables* (Vol. V, 1929, page 98). They are reproduced in Table V below after conversion from joules to calories.



TABLE II  
*Computation of specific heat*

	50° K.	75° K.	100° K.	125° K.	150° K.	175° K.	200° K.	225° K.
3E (490)	0.0001	0.0049	0.0300	0.0805	0.1465	0.2163	0.2824	0.3414
4E (463)	0.0002	0.0100	0.0529	0.1315	0.2281	0.3254	0.4144	0.4921
8E (446)	0.0007	0.0255	0.1258	0.2984	0.5016	0.7003	0.8789	1.0325
6E (423)	0.0010	0.0269	0.1189	0.2643	0.4258	0.5784	0.7114	0.8240
4E (400)	0.0011	0.0252	0.0993	0.2069	0.3202	0.4228	0.5105	0.5830
8E (387)	0.0031	0.0605	0.2253	0.4525	0.6841	0.8900	1.0629	1.2049
3E (365)	0.0020	0.0310	0.1038	0.1965	0.2858	0.3625	0.4255	0.4764
3E (313)	0.0067	0.0629	0.1649	0.2715	0.3624	0.4347	0.4909	0.5342
6E (277)	0.0302	0.1993	0.4432	0.6653	0.8405	0.9729	1.0717	1.1463
3D (277)	0.1003	0.2420	0.3700	0.4647	0.5315	0.5787	0.6125	0.6372
Mol. heat	0.1454	0.6882	1.7341	3.0321	4.3265	5.4820	6.4611	7.2720
Sp. heat	0.0036	0.0171	0.0430	0.0752	0.1073	0.1360	0.1602	0.1804

A comparison of the figures appearing in Table V with the calculated specific heats at the nearest temperatures appearing in Tables II, III and IV shows that the variation of specific heat with temperature as actually measured is well represented by the theoretical computations. The excellence of the agreement is made clearer in Fig. 1 below where the theoretical curve is drawn as a continuous line while the dots represent the experimental data.

At the lowest temperature of 50° K. listed in Table II, the contribution of the residual spectrum to the specific heat forms the largest part of the whole. But as the temperature rises, its relative importance diminishes rapidly, being only 1/5th of the whole at 100° K. and 1/10th at 200° K. It thereafter diminishes progressively to its limiting value of 1/16th. These changes are a consequence of the continued increase with rising temperature of the contributions of the discrete frequencies to the specific heat, while



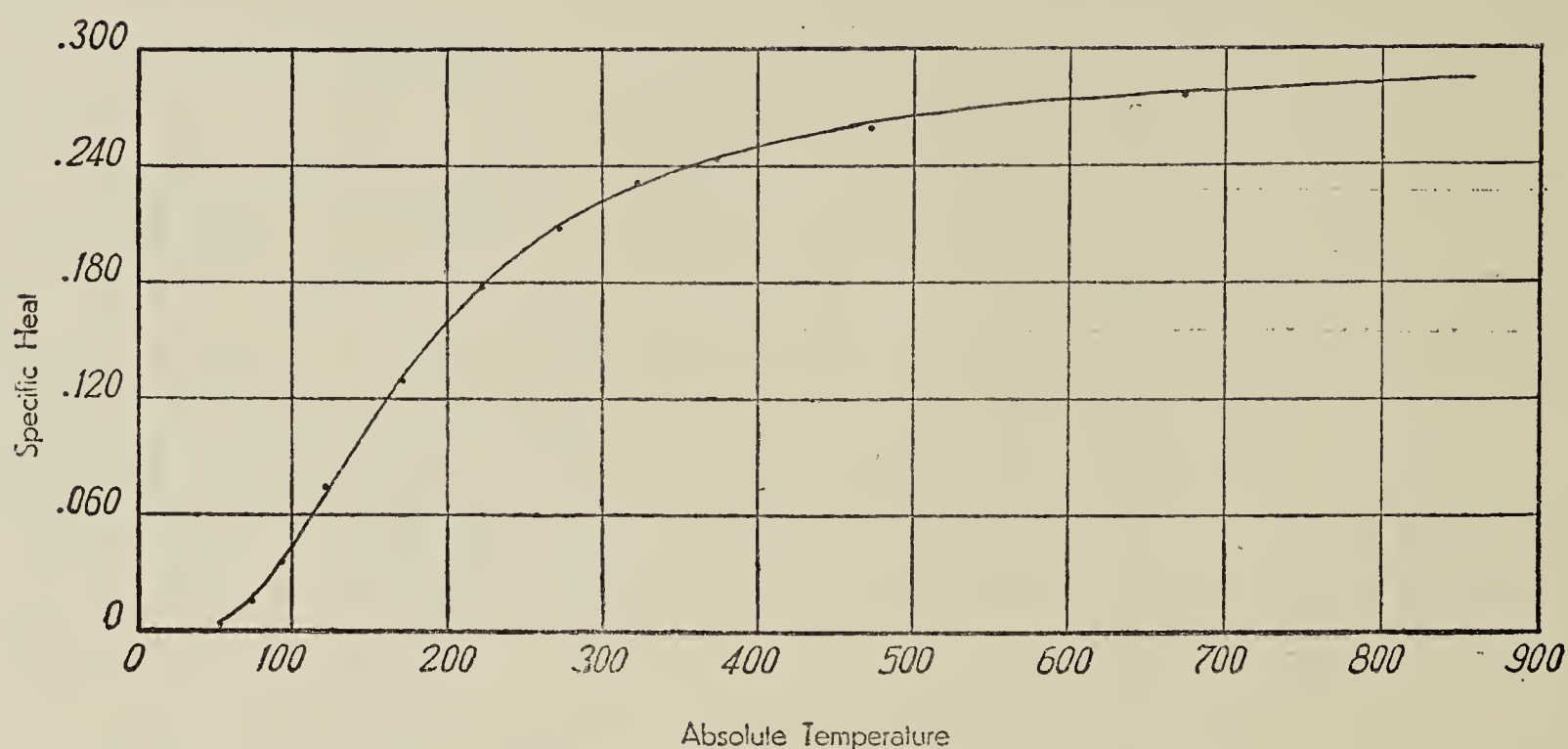


FIG. 1. Specific heat of MgO.

Calculated —————  
 Observed ●●●●●

TABLE III  
*Computation of specific heat*

	250° K.	275° K.	300° K.	350° K.	400° K.	450° K.	500° K.
3E (490) ..	0.3926	0.4364	0.4736	0.5321	0.5746	0.6059	0.6297
4E (463) ..	0.5586	0.6146	0.6616	0.7346	0.7870	0.8258	0.8547
8E (446) ..	1.1620	1.2708	1.3612	1.5007	1.6000	1.6731	1.7283
6E (423) ..	0.9178	0.9952	1.0591	1.1568	1.2259	1.2764	1.3122
4E (400) ..	0.6428	0.6913	0.7313	0.7916	0.8336	0.8648	0.8869
8E (387) ..	1.3205	1.4146	1.4906	1.6059	1.6867	1.7429	1.7892
3E (365) ..	0.5171	0.5500	0.5765	0.6163	0.6439	0.6627	0.6790
3E (313) ..	0.5680	0.5946	0.6161	0.6475	0.6690	0.6841	0.6949
6E (277) ..	1.2035	1.2481	1.2832	1.3340	1.3692	1.3929	1.4109
3D (277) ..	0.6558	0.6700	0.6811	0.6971	0.7079	0.7154	0.7208
Mol. heat ..	7.9387	8.4850	8.9343	9.6166	10.0978	10.4440	10.7066
Sp. heat ..	0.1969	0.2104	0.2216	0.2385	0.2504	0.2590	0.2655



TABLE IV  
*Computation of specific heat*

	550° K.	600° K.	650° K.	700° K.	750° K.	800° K.	850° K.
3E (490)	0.6483	0.6615	0.6754	0.6835	0.6906	0.6969	0.7022
4E (463)	0.8757	0.8952	0.9088	0.9191	0.9282	0.9358	0.9423
8E (446)	1.7673	1.8054	1.8281	1.8482	1.8652	1.8799	1.8915
6E (423)	1.3440	1.3653	1.3821	1.3961	1.4079	1.4176	1.4255
4E (400)	0.9058	0.9180	0.9286	0.9371	0.9442	0.9500	0.9547
8E (387)	1.8210	1.8451	1.8649	1.8815	1.8943	1.9053	1.9141
3E (365)	0.6890	0.6975	0.7044	0.7097	0.7141	0.7176	0.7207
3E (313)	0.7033	0.7097	0.7144	0.7187	0.7221	0.7247	0.7269
6E (277)	1.4239	1.4340	1.4421	1.4486	1.4536	1.4581	1.4616
3D (277)	0.7247	0.7279	0.7303	0.7323	0.7338	0.7352	0.7362
Mol. heat	10.9030	11.0596	11.1791	11.2748	11.3540	11.4211	11.4757
Sp. heat	0.2704	0.2743	0.2773	0.2796	0.2816	0.2833	0.2846

TABLE V  
*Measured specific heats of MgO*

Absolute temperatures ..	53°	73°	93°	123°	173°	223°
Specific heats ..	0.0033	0.0158	0.0358	0.0741	0.1290	0.1768
Absolute temperatures ..	273°	323°	373°	473°	673°	873°
Specific heat ..	0.2078	0.2317	0.2437	0.2604	0.2771	0.2915

on the other hand, the contribution of the residual spectrum soon reaches its limiting value. It will be noticed from Tables II and III that E (277) and D (277) become nearly equal to each other at temperatures higher than 250° absolute. This is a consequence of the fact that the vibrational modes



appearing in the residual spectrum are clustered near its upper limit of frequency. This is equivalent to stating that the residual spectrum arises for the most part from internal oscillations in volume elements whose dimensions are not very much larger than those of the dynamic units in the crystal. A great majority of them may be about four times as large in each direction as the unit cells of the crystal structure. Only at the very lowest temperatures, when the modes of higher frequencies cease to be excited, would any appreciable part of the thermal energy be ascribable to oscillators of still larger sizes.

### 5. SUMMARY

The specific heat of MgO at various temperatures from 50 to 850° absolute is computed by adding up the Einstein functions corresponding to the nine modes with discrete frequencies indicated by the dynamical theory and confirmed by infra-red spectroscopy. To this is added the contribution from a residual spectrum of vibrations of lower frequencies, the existence of which is also indicated by the dynamical theory. A very satisfactory agreement emerges over the whole range of temperatures between the calculated and observed specific heats.



# THE SPECTROSCOPIC BEHAVIOUR OF ROCK-SALT AND THE EVALUATION OF ITS SPECIFIC HEAT

## Part I. The Structure and Its Free Vibrations

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### 1. INTRODUCTION

SODIUM CHLORIDE, as is well known, crystallises in the cubic system and is therefore optically isotropic. If the material is pure, the crystals are colourless and transparent over a wide range of wavelengths in the spectrum. The absorption is negligible between  $0.2\mu$  and  $10\mu$ , and is quite small between  $10\mu$  and  $15\mu$ , but increases rapidly as we proceed further out into the infra-red. The technical possibility of preparing crystals of the material in large sizes from melts and of cutting out prisms from such material has made rock-salt play a highly important role in the development of infra-red spectroscopy. The range of wavelengths covered by recording instruments using NaCl prisms is from  $1\mu$  to  $15\mu$ .

The simplicity of the composition and structure of rock-salt and the ready availability of the material make its physical properties, including especially its optical and spectroscopic behaviour, matters of very great interest from a theoretical point of view. Quite naturally, therefore, a great volume of literature exists describing the results of experimental studies and also of theoretical discussions concerning these matters. In the present memoir we are concerned with the spectroscopic behaviour of rock-salt in the region of infra-red wavelengths and its relation to the crystal structure and thermal properties of the material. It is, therefore, appropriate that we briefly recall here the major facts which have emerged from the experimental researches on the subject.

Three different methods are available for the study of the spectroscopic behaviour of rock-salt in the region of infra-red wavelengths. The first is that of determining the variation of the reflecting power of rock-salt in the region of great wavelengths. Earlier investigations indicated that the



reflecting power is quite small up to about  $35\mu$  and that it commences to rise steeply beyond  $40\mu$ . It exceeds 80% between  $50\mu$  and  $55\mu$ , and then drops to 70% at  $60\mu$  and to 40% at  $70\mu$ . The further diminution at still greater wavelengths is relatively more slow. The more recent investigations indicate a reflecting power greater than 90% between  $50\mu$  and  $56\mu$ , and also reveal additional features in the region of lower wavelengths which will be referred to later.

The second method is the study of the absorption of infra-red radiation in its passage through the material. The spectral transmission curve depends very much on the thickness of material traversed. The absorption coefficient which is small at  $15\mu$  increases more and more steeply with increasing wavelength as we approach the region in which the reflecting power becomes large. In the latter region, the cut-off due to the reflection at the two surfaces of the plate is superposed upon the loss due to absorption. To obtain any sensible transmission in this region, very small thicknesses of the material are needed. Very interesting results were obtained and reported by Czerny (1930). Mentzel (1934) observed that the curve of percentage transmission through a rock-salt plate  $24\mu$  thick showed an arrest between  $34.5\mu$  and  $35.5\mu$ , the curve running horizontally between these wavelengths though it goes down steeply with increasing wavelength both above and below this range. Barnes and Czerny (1931) found that the curve of transmission through a plate  $8\mu$  thick likewise runs horizontally in the wavelength range between  $40\mu$  and  $44\mu$ . These authors also studied the transmission through evaporated films of NaCl of various thicknesses between  $3.6\mu$  and  $1.35\mu$ . The percentage transmission exhibited as a graph in their paper shows two downward dips located at  $40\mu$  and  $50\mu$  respectively, besides the highly pronounced minimum of transmission around  $60\mu$ . The thinner films showed a further small dip in the transmission curve at about  $71\mu$ . Mentzel in his paper listed  $34\mu$ ,  $40.5\mu$  and  $51\mu$  as minor maxima of absorption and  $61.1\mu$  as the major absorption wavelength for NaCl. He also listed  $33\mu$ ,  $41\mu$ ,  $42.5\mu$ ,  $47\mu$  and  $60\mu$  as minor absorption peaks and  $70.7\mu$  as the major absorption wavelength for KCl. The appearance of a whole series of minor absorption peaks is thus evidently a characteristic feature of the spectroscopic behaviour of the alkali halides.

A third and very powerful method for the study of the spectroscopic behaviour of rock-salt was initiated and employed by Rasetti (1931). The transparency of the crystal in the ultra-violet region enables the powerful  $2536.5\text{ \AA}$  radiation emitted by a water-cooled and magnet-controlled mercury arc to be used for illuminating the interior of the solid and for recording



the spectrum of the scattered radiation emerging from its interior. Rasetti made the noteworthy discovery that the spectrum thus recorded exhibits a sharp and intense line with a wave-number shift of  $235\text{ cm.}^{-1}$  from the exciting radiation. This is the most conspicuous feature observed in the spectrum which commences with a sharp rise in intensity from zero to a large value at the wave-number shift at  $360\text{ cm.}^{-1}$  and extends towards smaller frequency-shifts. The drop of intensity beyond the sharply-defined peak of the line at  $235\text{ cm.}^{-1}$  to zero in the region of smaller frequency shifts is also quite steep but is broken by the presence of a feeble band which covers the region of frequency-shifts between  $220\text{ cm.}^{-1}$  and  $184\text{ cm.}^{-1}$ . The upper end of the spectrum exhibits a peak of intensity which is both smaller and not so well defined as the line at  $235\text{ cm.}^{-1}$  and covers the region of frequency-shifts between  $360\text{ cm.}^{-1}$  and  $340\text{ cm.}^{-1}$ . Clearly separated from both of these principal features in the spectrum and approximately midway between them appears a group of four maxima of intensity located respectively at the frequency-shifts of  $314\text{ cm.}^{-1}$ ,  $300\text{ cm.}^{-1}$ ,  $280\text{ cm.}^{-1}$  and  $258\text{ cm.}^{-1}$ . These are clearly separated from each other in the spectrum as well as in its microphotometer record.

It is proposed in this memoir to consider the spectroscopic behaviour of rock-salt in its fundamental aspects and also in relation to its activity in infra-red absorption and reflection and its activity in the scattering of light with change of frequency. A satisfactory explanation is given for the facts established by experimental study in both of these fields of research. The thermal energy content of rock-salt and the variation of its specific heat with temperature also receive a quantitatively satisfactory explanation in terms of the spectroscopic properties of the crystal.

## 2. THE STRUCTURE OF ROCK-SALT

All crystals may be described as assemblages of two kinds of particles differing in their nature and properties, being respectively the heavy positively charged nuclei and the light negatively charged electrons. These two types of particles by reason of their mutual interactions hold each other in place and form a regularly arranged grouping in space. The massive nuclei are located at specific points in the structure but are capable of executing oscillatory movements about those positions. On the other hand, since the mass of the electrons is very small, they are appropriately described as forming a cloud which envelops the nuclei and fills up the volume of the solid. The attraction of a nucleus on the electrons in its immediate vicinity results in a closer association between them. As a consequence, the field due to



each positive charge is more or less completely cancelled out at a distance from it. Part of the electronic cloud however remains subject to the influence of more than one nucleus and this plays a highly important role in holding the crystal together as a coherent solid. The physical properties of the crystal and especially its spectroscopic behaviour in the lower ranges of frequency are largely determined by it.

The numbers of Na and Cl nuclei in rock-salt are equal and their dispositions in the structure are very similar. The usual description of the structure is that it consists of two interpenetrating face-centred cubic lattices, the points of which are occupied respectively by Na and Cl nuclei. Each Na nucleus appears surrounded by six Cl nuclei and each Cl nucleus by six Na nuclei, the distance between the nearest neighbours being one-half of the edge-length of the cubic cell as measured from one Na nucleus to the next or from each Cl nucleus to the next. In the atomic layers parallel to the cubic faces of the crystal, the Na and the Cl nuclei appear interspersed in such manner that each Na nucleus has four Cl nuclei as its immediate neighbours, while each Cl nucleus has four Na nuclei similarly situated with respect to it. On the other hand, in the atomic layers which are equally inclined to all the cubic axes, in other words are parallel to the faces of the octahedron, the Na nuclei and Cl nuclei do not appear together but are located in separate but equidistant layers. The distance  $a$  between neighbouring Na and Cl nuclei is also the spacing of successive atomic layers parallel to the cubic faces, while the separation of each Na layer from either of the two Cl layers adjacent to it in the octahedral planes is  $a/\sqrt{3}$ .

The structure of rock-salt may also be described as arising from the juxtaposition of two rhombohedral lattices displaced with respect to each other, the points of the two lattices being occupied respectively by Na and by Cl nuclei. Eight nuclei occupying the corners of a rhombohedron delineate the cells of each lattice. Six of them are located at the face-centres of a cube while the remaining two are located at opposite cube-corners.

### 3. THE FREE VIBRATIONS OF THE STRUCTURE

The atomic nuclei being enormously more massive than the electrons, it is permissible, when we seek to find and enumerate the normal modes of vibrations of the nuclei about their positions of equilibrium in the structure, to regard the electrons as being in the nature of massless elastic springs holding the nuclei in their places. Since the crystal also consists of an enormous number of similar and similarly situated structural units each containing its quota of atomic nuclei which is the same for all the structural units, we



may justifiably adopt the following procedure in dealing with the problem. We proceed on the basis of the theorem in the classical mechanics which states that the small vibrations of a system of connected particles about their positions of equilibrium are a summation of a set of normal modes in each of which all the particles of the system vibrate in the same or opposite phases, while the total number of normal modes is the same as the number of degrees of dynamical freedom of the system of particles. It follows that the vibrations of the atomic nuclei should satisfy the following two requirements: in any normal mode, the nuclei should all vibrate in the same or opposite phases: a normal mode should remain a normal mode following a unit translation of the crystal along any one of the three axes of the crystal structure. Taking these two principles together, it follows as a necessary consequence that following a unit translation of the crystal, the atomic nuclei in the structural unit would retain the same amplitudes of vibration while their phases would either *all* remain unaltered or else would *all* be reversed. Thus, we have two species of normal modes satisfying the requirements for each of the three axes of the structure, and since these possibilities are independent, we have  $2 \times 2 \times 2$  or 8 species of normal modes in all.

We may readily apply these results to the case of a simple rhombohedral lattice at whose points only one kind of nucleus is located. Each of the 8 species of normal modes corresponds to a different disposition of the phases of vibration of the 8 nuclei situated at the corners of the cell. As each nucleus has three degrees of dynamical freedom, we have 24 available degrees of freedom. The nature of the 24 different possible movements allowed by these degrees of freedom can be readily ascertained by considering the different combinations of the phases of vibrations of the nuclei located at the points of the rhombohedral lattice. Three of them are movements of all the nuclei in the same phase, in other words, simple translations of the whole group of nuclei. Nine of them represent movements in which the nuclei lying in the same cubic plane move in the same phase while those in the adjoining cubic planes move in the opposite phase. The remaining twelve represent movements in which the nuclei lying in the same octahedral plane move in the same phase while those lying in the adjacent octahedral plane move in the opposite phase. These two groups may be further subdivided by considering the directions of movement indicated by the cubic symmetry of the whole structure. Thus the 24 possible movements may be listed as below, it being noted that the oscillations of the nuclei located in the successive planes (cubic or octahedral as the case may be) are in opposite phases.



1. Simple translations	..	..	..	..	..	3
2. Oscillations normal to the cubic planes	..			..	..	3
3. Oscillations tangential to the cubic planes				..	..	6
4. Oscillations normal to the octahedral planes				..	..	4
5. Oscillations tangential to the octahedral planes				..	..	8
				Total	..	<u>24</u>

Thus, the 24 degrees of dynamical freedom of the group of 8 nuclei located at the corners of the rhombohedral cell are duly accounted for, 3 of them as simple translations and the remaining 21 as normal modes which fall into four groups with degeneracies 3, 6, 4 and 8 respectively, arising by reason of the cubic symmetry of the structure.

In the rock-salt structure we are concerned with two sets of nuclei (Na and Cl respectively) occupying the points of two similar rhombohedral lattices. Hence the foregoing description would apply to each of them. The phases of oscillation of the Na and Cl nuclei in each of the 24 modes may either be the same or opposite. Hence, we have 48 normal modes in all, corresponding to the 48 degrees of dynamic freedom of a group of 16 nuclei, 8 of Na and 8 of Cl. The three translations of each lattice separately are replaced by three translations in which the two lattices move together in the same phase, and by three oscillations respectively along the three cubic axes of the two lattices moving in opposite phases, the movement of the Na nuclei being balanced by the movement of the Cl nuclei in the contrary direction. Besides these, we have *four modes* which are coupled oscillations of the Na and Cl nuclei, two being normal and two tangential to the cubic planes with the Na and the Cl nuclei in those planes moving respectively in the same or in the opposite phases with respect to each other; also *four modes* in which the *Na nuclei alone* or the *Cl nuclei alone* present in the octahedral planes oscillate respectively normal and tangential to those planes.

#### 4. THE NORMAL MODES OF VIBRATION

The nine normal modes of vibration and the three residual translations are listed below as a table;



			Degeneracy
I.	Oscillation of the Na and Cl lattices in opposite phases ..		3
II.	Coupled oscillations of the Na and Cl nuclei in the cubic planes:		
	(a) Tangential to the planes in opposite phases .. ..	6	
	(b) Normal to the planes in the same phase .. ..	3	
	(c) Normal to the planes in opposite phases .. ..	3	
	(d) Tangential to the planes in the same phase .. ..	6	
III.	Oscillations of the nuclei appearing in the octahedral layers		
	(a) Na nuclei normal to the planes .. ..	4	
	(b) Na nuclei tangential to the planes .. ..	8	
	(c) Cl nuclei normal to the planes .. ..	4	
	(d) Cl nuclei tangential to the planes .. ..	8	
IV.	Translations of both lattices in the same phase .. ..	3	
	Total ..	48	

The nine modes have been numbered and shown in the table in a particular order for reasons which will presently be explained. Figures 1, 2 and 3 in the text below illustrate the character of the oscillations in each

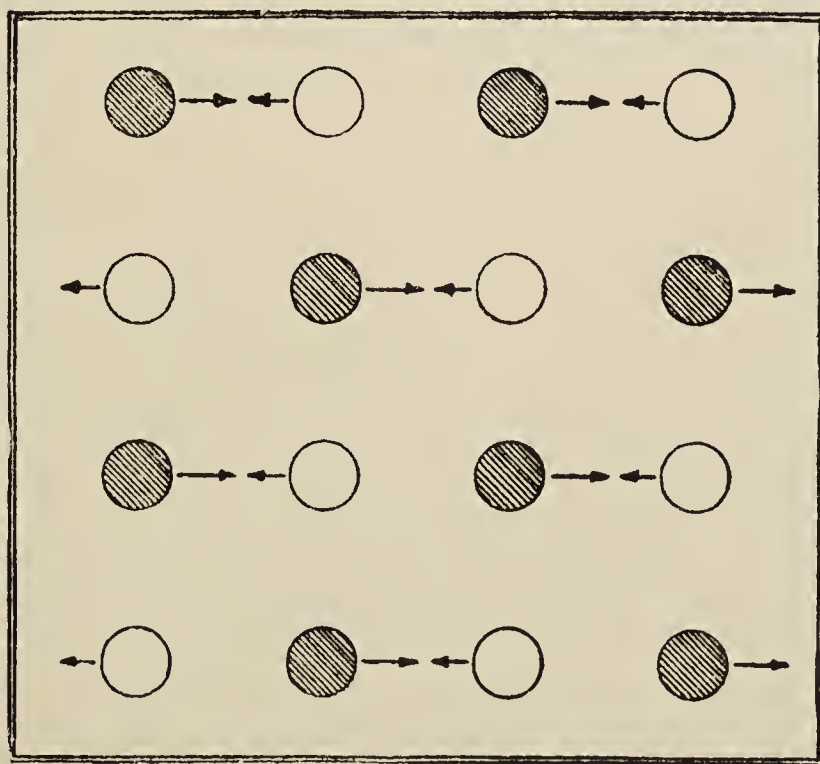


FIG. 1. Oscillation of the Na and the Cl lattices in opposite phases,



case, the numbering of the figures following the same order as in the table. The hatched circles represent the Na nuclei and the open circles the Cl nuclei. Figures 1 and 2 represent the structure viewed along a cubic axis; the cubic layers depicted are assumed to be horizontal, and the arrows represent the movements of the nuclei. Figure 3 is a view of the structure in a direction which is the intersection of an octahedral plane with a diagonal plane of the cube. It exhibits the Na and the Cl nuclei as appearing in distinct layers parallel to the faces of the octahedron.

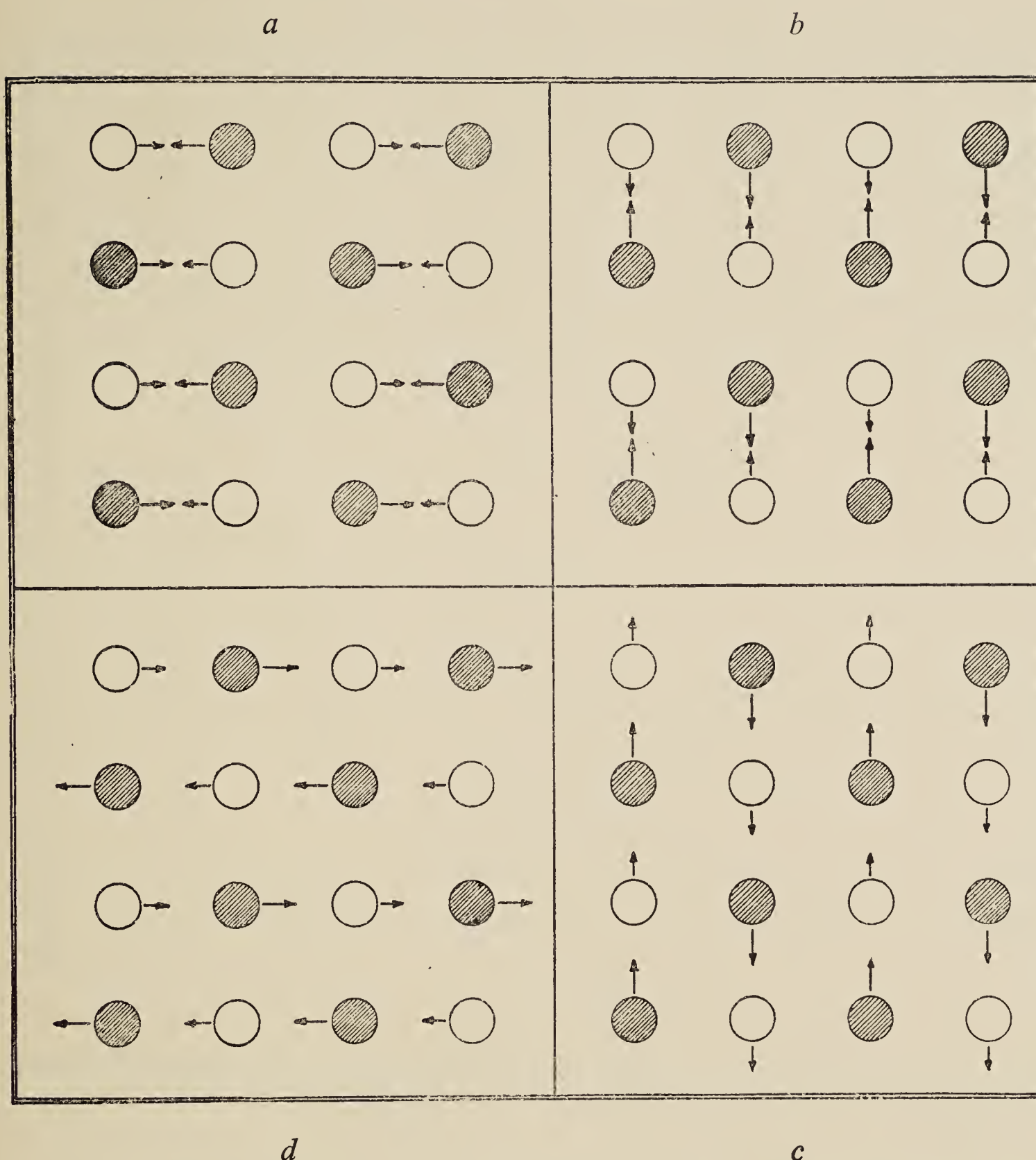
### 5. THE FREQUENCIES OF THE NORMAL MODES

It would obviously be useful if the nine modes of vibration described and pictured above can be arranged in descending order of frequency, as this would greatly facilitate the comparison with the spectroscopic data and a definitive determination of their frequencies.

The mode illustrated in Fig. 1 evidently stands apart in a category by itself. This oscillation repeats itself from cell to cell, whereas in all the other eight modes the phase of vibration alternates from layer to layer. It may therefore be safely presumed that Fig. 1 represents the mode of highest frequency. The coupled oscillations of the Na and Cl nuclei in the cubic planes have been listed and pictured in the order of Figs. 2 (*a*), (*b*), (*c*) and (*d*). This would clearly also represent their arrangement in descending order of frequency. For, the movement in Fig. 2 (*a*) most closely resembles that in Fig. 1 and the movement in Fig. 2 (*b*) rather less closely, while the movements in Figs. 2 (*c*) and 2 (*d*) are clearly of a different nature. Indeed, Fig. 2 (*d*) closely resembles a transverse oscillation of the cubic layers as a whole and hence should have the lowest frequency of the four modes and indeed also of all the nine modes.

Since the masses of the Na nuclei are much smaller than of the Cl nuclei, it is evident that the modes depicted in Figs. 3 (*a*) and 3 (*b*) would both have higher frequencies than the modes shown as Figs. 3 (*c*) and 3 (*d*). The mode shown as Fig. 3 (*a*) would evidently have a higher frequency than the mode shown as Fig. 3 (*b*), since the Na layers approach each other normally in one case and move tangentially to each other in the other case. Likewise, the frequency of mode III (*c*) would be higher than that of mode III (*d*). But the differences between the normal and tangential modes in either case would not be very large for the reason that the six nearest neighbours of each oscillating nucleus are situated symmetrically around it and hence its interactions with them would be the same in both cases.





FIGS. 2 (a), (b), (c) and (d). Coupled oscillations of the Na and Cl nuclei in the cubic layers.

## 6. APPROXIMATE EVALUATION OF THE FREQUENCIES

We may go a little further and make a rough computation of the frequencies of all the nine modes on the basis of a simplified picture of the internuclear forces which are operative in a vibration. We notice that in Fig. 1 the movements are along a cubic axis of the crystal and represent an approach of a Na nucleus to the Cl nucleus which is its nearest neighbour on one side and a recession from the Cl nucleus on the other side. (We may interchange the Na and the Cl nuclei in this description.) The forces brought into play would be principally those resisting such approach or



recession. Of lesser importance would be those resisting the transverse displacement of each Na nucleus with respect to the four other Cl nuclei which are also its nearest neighbours on the perpendicular cubic axes. We shall assume these forces to be respectively proportional to the relative displacements, the constants of proportionality being  $\alpha$  and  $\beta$  respectively. We neglect all other interactions. Such neglect is fully justified as regards interactions with more distant nuclei *of the same species*, since they move with the same amplitudes and phases. Writing down the equations of motion of two adjoining nuclei (Na and Cl respectively) and solving them, we find that the circular frequency of the vibrational mode I is given by

$$\omega_I^2 = (2\alpha + 4\beta)(1/m_1 + 1/m_2),$$

where  $m_1$  and  $m_2$  are respectively the masses of the Na and Cl nuclei.

Considering only the interactions between each Na nucleus and the surrounding six Cl nuclei, *and vice versa*, the equations of motion may be written down and solved for the two modes represented in Figs. 2(a) and 2(d). The circular frequencies of these modes may be found on evaluating the two roots of the equation which is obtained as the solution, *viz.*,

$$\omega_{II}^4 - \omega_I^2 \cdot \omega_{II}^2 + 16\beta(\alpha + \beta)/m_1m_2 = 0.$$

Likewise, on the same basis, the equations of motion for the two modes represented by Figs. 2(b) and 2(c) may be written down and solved. Their circular frequencies may be found from the two roots of the equation

$$\omega_{II}^4 - \omega_I^2 \cdot \omega_{II}^2 + 32\alpha\beta/m_1m_2 = 0.$$

It will be noticed from these equations that the frequencies of the two coupled oscillations in each case are related to the frequency  $\omega_I$  of mode I by the simple relations

$$\omega_{II} a^2 + \omega_{II} d^2 = \omega_I^2$$

and

$$\omega_{II} b^2 + \omega_{II} c^2 = \omega_I^2.$$

It is evident also from these relations that mode I has the highest frequency of all the five modes considered. They can all be computed if the values of  $\alpha$  and  $\beta$  are known. Alternatively, if the frequency of mode I is known and some reasonable assumption is made for the ratio  $\alpha/\beta$ , as for example that  $\alpha = 2\beta$ , the frequencies of the four other coupled oscillations of the Na and Cl nuclei can be found from that of the mode of highest frequency,



Assuming that the frequency of mode I expressed in wave-numbers is  $180 \text{ cm.}^{-1}$  and that  $\alpha = 2\beta$ , we find the following values for the frequencies of the four other modes also in wave-numbers:

Frequency of mode I (assumed)	..	..	$180 \text{ cm.}^{-1}$
Frequency of mode II ( <i>a</i> ) (calculated)	..	..	$158 \text{ cm.}^{-1}$
Frequency of mode II ( <i>b</i> ) (calculated)	..	..	$140 \text{ cm.}^{-1}$
Frequency of mode II ( <i>c</i> ) (calculated)	..	..	$113 \text{ cm.}^{-1}$
Frequency of mode II ( <i>d</i> ) (calculated)	..	..	$87 \text{ cm.}^{-1}$

Thus, the descending sequence of frequency in which these five modes were arranged in the table and numbered in the figures is seen to be correct. It should be remarked however that the calculations ignored the interactions between each nucleus and the others of the same species present in the adjacent layers and moving with the same amplitude but in an opposite phase. As these nuclei are however situated further from it than the nuclei whose interactions have been considered, the calculations of frequency cannot be seriously in error. But they can only be considered only as approximations.

Considering now the four modes pictured as Figs. 3 (*a*), (*b*), (*c*) and (*d*) it is obvious that their frequencies would be very simply related to that of mode I, provided that we take into account only the interactions between each Na nucleus and the six Cl nuclei around it, and *vice versa*. The relevant formulæ are:

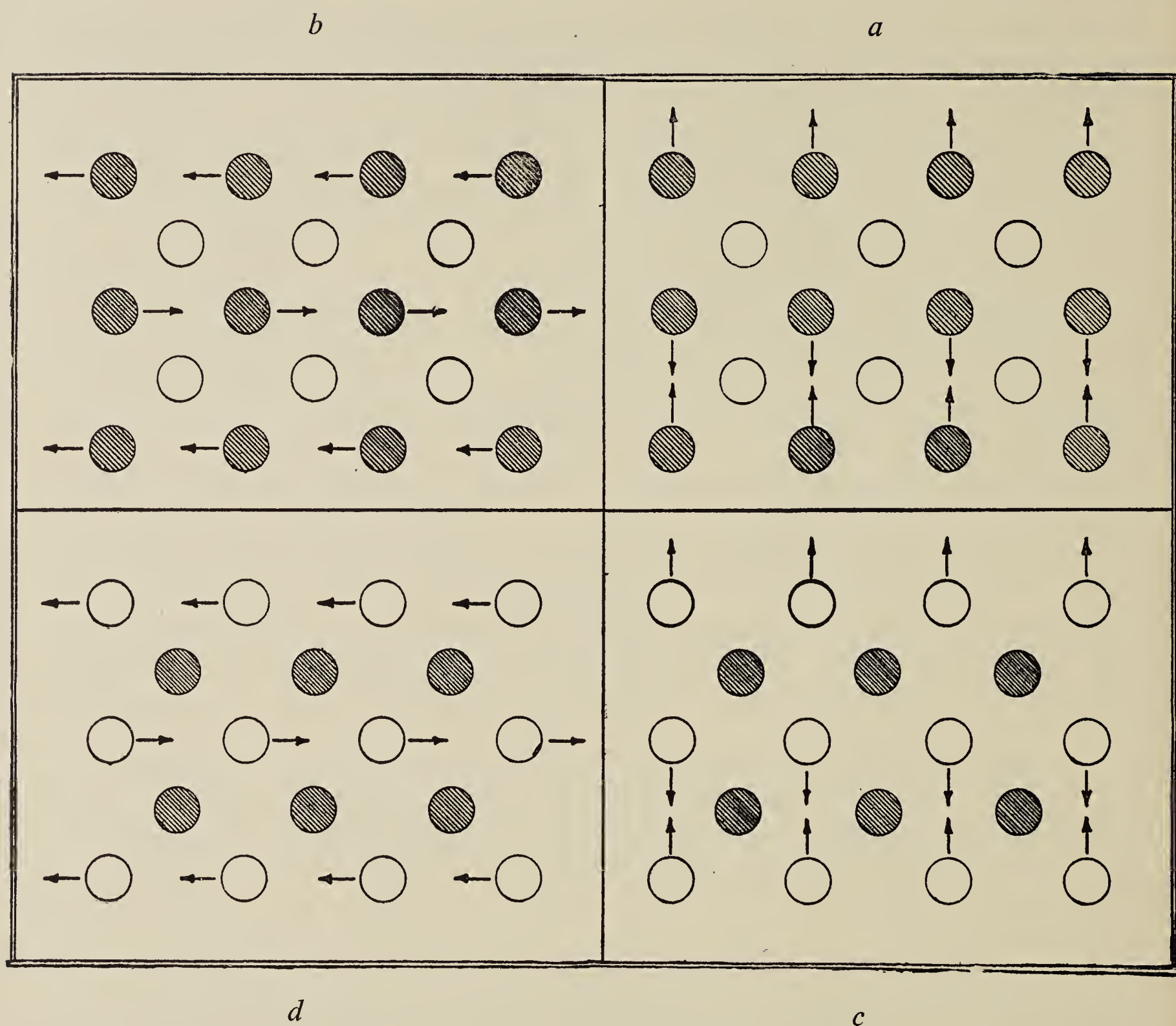
$$\omega_{\text{III}}^2 = (2\alpha + 4\beta)/m_1$$

for the modes III (*a*) and III (*b*) and

$$\omega_{\text{III}}^2 = (2\alpha + 4\beta)/m_2$$

for modes III (*c*) and III (*d*). If we take the frequency of mode I as  $180 \text{ cm.}^{-1}$  in wave-numbers, that of modes III (*a*) and III (*b*) come out as  $140 \text{ cm.}^{-1}$  and that of modes III (*c*) and III (*d*) as  $113 \text{ cm.}^{-1}$ . This procedure for deducing the frequencies results in the modes of vibration tangential and normal to the octahedral planes having the same value. This is a consequence of our having neglected the interactions between the nuclei of the same kind which are in relative movement and hence would influence the frequencies of the vibration. As will be seen from Figs. 3 (*a*), (*b*), (*c*) and (*d*), the adjacent layers of similar nuclei slide past each other in the tangential modes, while they alternately approach and recede from each other in the normal modes. The interactions between the moving layers would, in these circumstances, not be negligible. Their influence on the frequencies





FIGS. 3 (a), (b), (c) and (d). Oscillations of the Na and the Cl nuclei in the octahedral layers.

of vibration would evidently be greater in the normal modes than in the tangential ones, thereby making the frequencies in these cases different. It is also evident that the frequencies of  $140\text{ cm.}^{-1}$  and  $113\text{ cm.}^{-1}$  as computed and shown above would be slightly smaller than the correct values for the tangential modes, and definitely less than the correct values for the normal modes. Each moving nucleus comes under the influence of six nuclei of the same kind and six nuclei of the other kind in its movement, the distances between the interacting nuclei being  $2a/\sqrt{3}$  and  $a$  respectively. In these circumstances, an increase of say 10% in the frequencies of the tangential modes and say 20% in the frequencies of the normal modes may be hazarded



as a rough estimate of an alteration in the calculated frequencies produced by taking the interactions between like nuclei also into account.

## 7. SUMMARY

The nine normal modes of free vibration of the rock-salt structure have been deduced theoretically and fully described. They have been arranged in descending order of frequency and an approximate estimate of their frequencies is also given. The mode of highest frequency is that in which the Na and Cl lattices oscillate in opposite phases.

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- |                   |  |
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# THE SPECTROSCOPIC BEHAVIOUR OF ROCK-SALT AND THE EVALUATION OF ITS SPECIFIC HEAT

## Part II. Its Infra-Red Activity

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### 1. INTRODUCTION

THE basic questions in relation to the infra-red activity of crystals are, *firstly*, how does the activity arise and *secondly* how is it related to the structure of the crystal? Since these two questions are closely connected, it is evident that answers to them could most appropriately be sought for in relation to crystals of the simplest possible structure and composition and of the highest possible symmetry. For, the various complications such as those arising from the details of molecular structure, molecular anisotropy and molecular interactions would be avoided and the questions requiring answer would present themselves in the most definite and tractable form. It is also essential that the case considered is one which could be most completely explored by spectroscopic methods and experimental data obtained which could be compared with the consequences of theory. NaCl is a case in which these requirements are satisfied and hence is very suitable as a test-case.

Infra-red activity manifests itself in three different ways which are susceptible of experimental study. Firstly, we have the refractivity of the material which as we pass from the visible into the infra-red region clearly exhibits the effect of infra-red activity. Secondly, we have the reflecting power of crystal surfaces, and thirdly, the absorption of radiation in its passage through the material. The absorption is a mass-effect and where it is very powerful as in the case of rock-salt, we could scarcely expect studies of it to reveal its relationship to the spectroscopic behaviour in an obvious fashion. It is indeed necessary to obtain spectrographic records of the percentage transmission by plates whose thickness is varied step by step over the widest possible range and to make a comparative study of the records in order to obtain any useful indications.



In the present memoir, we shall cover various aspects of the subject. Firstly, we shall consider it from a purely fundamental and general standpoint. Secondly, we shall discuss the relation between infra-red activity and the free vibrations of the structure as considered in the first part of the memoir. Thirdly, the results of experimental studies of the kind indicated in the foregoing paragraph will be presented. Lastly, these experimental results will be correlated with those of Czerny and collaborators mentioned in the first part of the memoir and then compared with the consequences of theory.

## 2. THE ORIGIN OF INFRA-RED ACTIVITY

Viewed from the point of view of classical mechanics, the absorption of infra-red waves in their passage through a crystal can be considered as a transfer of energy which is effected by the electric field of the waves acting on the charged particles in its structure and setting them in vibration. If the frequency of the field is sufficiently close to the frequency of a normal mode of vibration, the possibility of resonance arises. But whether such resonance would actually occur is a question that needs examination.

As there are two types of charged particles in the structure, *viz.*, the nuclei and the electrons, it is appropriate at first to consider the effects of the radiation field on them separately. The nuclei besides being positively charged possess masses enormously large compared with those of the electrons. It is a familiar consequence of classical mechanics that in a normal vibration the common centre of inertia of the particles of the system remains at rest. Likewise, in our present problem, the common centre of inertia of all the nuclei included in the vibrating structural unit would remain at rest in any free vibration. Hence, when all the nuclei have the same mass, as for example, in a crystal of diamond or silicon or germanium, the common centre of the positive charges carried by the nuclei would remain undisturbed during the vibration. It follows that when the crystal is traversed by infra-red radiation, the forces exerted by the field on the positive charges would in the sum total be unable to transfer energy to the crystal and hence they could not possibly excite such vibrations. The situation would be the same even when the nuclei in the crystal belong to different species, provided that the ratio of the masses to the charges is the same for the different nuclei, as is the case for example with rock-salt or quartz. It follows that the positive charges of the nuclei do not play any role in the infra-red activity of the crystals. *All the observed effects arise from the action of the field of incident radiation on the negatively charged electronic clouds.*



The question then arises why the infra-red absorption spectra of a crystal should be related in any way or bear any resemblance to the spectrum of free vibrations of the atomic nuclei considered in the first part of the present memoir. The answer to this is that there is a connecting link between the infra-red absorption and the vibration spectrum of the atomic nuclei. This is to be found in the fact that the electronic clouds are held in the crystal by their interactions with the positively charged nuclei; *vice versa*, the nuclei are held in their places by their interactions with the electronic clouds. Hence, a periodic disturbance of the electronic clouds produced by the field of the radiation *may* tend to disturb the nuclei from their positions and set them in synchronous vibration. *Vice versa*, vibrations of the nuclei *may* tend to disturb the electronic clouds and set them in synchronous vibration. A periodic movement of the electronic cloud is a *sine qua non* for the production of the effects described under the term of infra-red activity. Hence, unless a free vibration of the nuclei is associated with and gives rise to such a movement of the electronic clouds, it would not be set up under the action of the periodic external electric field.

The foregoing discussions, apart from emphasising the fundamental role played by the electrons in the absorption of infra-red radiation and other related effects, make it clear why the *asymmetry* of the nuclear vibrations plays such a highly important role in infra-red activity. For, in the absence of such asymmetry, there would be no periodic displacement of the electronic clouds and hence no excitation of the nuclear vibrations.

### 3. INFRA-RED ACTIVITY OF THE NORMAL MODES

From what has been stated in the preceding paragraph, it is clear that the four modes in which the Na nuclei alone or the Cl nuclei alone oscillate either normally or tangentially to the octahedral planes could not exhibit any infra-red activity. For, in these modes, two layers of Na nuclei approach or recede from an intermediate layer of Cl nuclei symmetrically on either side with equal amplitudes. Hence, the movements of electronic charges resulting therefrom when summed up over each of the structural elements of the crystal would vanish. This conclusion would be valid irrespective of the actual amplitude of the nuclear movements. Hence the four modes of the octahedral class can be disregarded in our consideration of the infra-red activity of the normal modes of vibration. We need only examine the behaviour of the five other normal modes in which the Na and Cl nuclei appearing in the cubic layers execute coupled oscillations.

The principal normal mode of highest frequency in which the Na and Cl lattices oscillate in a balanced movement stands in a class by itself



and will therefore be considered first. By reason of the difference in the masses of the Na and the Cl nuclei, the amplitude of movement of the Na nuclei would be proportionately greater than that of the Cl nuclei and hence the amplitudes of oscillation of the electronic clouds respectively held by them in close association would also be different. But by reason of the difference in the positive charges of the two nuclei, the negative charge of the electrons so held would be smaller for the Na nuclei than for the Cl nuclei. The resulting displacements of negative charge when totalled up would therefore cancel out more or less completely. What would be left over and needs special consideration is the part of the electronic cloud which comes under the influence of both sets of nuclei and its movements under the action of the field of incident radiation.

During one half-period of the oscillation, the Cl nucleus on one side of a Na nucleus approaches it and the Cl nucleus on the other side recedes from it. During the other half-period, these movements are reversed. It is clear, however, that the asymmetric displacements of electric charge with which we are here concerned would be in the same direction on both sides of the Na nucleus and that they would be reversed in successive half-periods of the oscillation. Hence, they would not cancel out but would add up to produce a periodic displacement of negative charge having the same frequency as the incident waves. Further, since the oscillation of the nuclei repeats itself from cell to cell, the effects of all the cells would add up and hence would result in a large effect. In other words, the normal mode of highest frequency would be powerfully infra-red active, and it would need only a very small thickness of the material to make such activity manifest. The coherent phase relationship between the oscillations of electric charge in the adjacent cells of the structure would have a further consequence. The oscillating electric charges at and near the surface of the crystal would act as secondary sources of radiation and their conjoint action would result in a powerful reflection of the incident radiation at the surface of the crystal. This effect would be most powerful at and near the frequency of the normal mode under consideration. For, at such frequencies, the movements of the nuclei would be most vigorous and hence the displacements of negative electric charge associated therewith would be large.

The four other modes of coupled oscillation of the Na and Cl nuclei stand on an entirely different footing. In these modes, the oscillation reverses its phase as it passes from one cubic layer of the crystal to the next. Hence, the displacements of electric charge would be in opposite phases in the alternate layers and when summed up would cancel each other out. Hence, these four normal modes would not exhibit any infra-red activity.



This statement is however subject to various qualifications, since it rests on two assumptions. The first assumption is the complete independence of the normal modes of vibration. The second assumption is that the amplitudes of vibration are extremely small. If these assumptions are not valid, the conclusion drawn that the four normal modes are inactive would also need reconsideration.

#### 4. OVERTONES OF THE NORMAL FREQUENCIES

So far, we have proceeded on the basis of the theory of small vibrations of a connected system of particles in the classical mechanics. The curious feature of the case is that the forces which are effective in exciting the vibrations are not those acting on the masses, *viz.*, the positively charged nuclei, but on the springs, *viz.*, the negatively charged electrons which hold them together and effectively determine their frequencies of vibration.

We have now, of necessity, to introduce the fundamental notions of the quantum theory. The energy of the radiation appears in quanta proportional to its frequency and if such energy is to be completely taken up by the oscillators with which we are concerned, *viz.*, the group of 8 Na and 8 Cl nuclei, the frequency of the mechanical oscillations should be the same as that of the incident radiation. In other words, we would have resonance. But we have also to consider the cases in which the frequency of the free vibration is not the same as that of the incident radiation. Of special interest are the cases in which the frequency of the incident radiation is a small multiple of the frequency of the oscillator, and hence the absorption of energy would involve the acceptance by the oscillator of two, three or larger number of quanta of the energy of radiation. It may be presumed that the probability of this happening would diminish rapidly with the increasing number of quanta thus taken up, in other words that the absorption would then become rapidly weaker and weaker in the series. But since we are dealing with a crystal, there should be no difficulty in observing such absorption. We have only to increase the thickness of the absorbing plate sufficiently to be able to record the absorption spectra of the higher orders.

The further question then arises, what is the factor which determines the diminishing strength of the absorption with the increasing number of quanta taken up by the oscillator? We may remark that an increase in the magnitude of the energy taken up involves an increase of the amplitude of the resulting vibration. The absolute dimensions of the oscillator being small, the amplitude of the movements corresponding only to one quantum of energy could by no means be considered as small, and the amplitude corresponding to two, three more quanta would far transcend any such



limits. The movements of the electronic clouds which are the operative cause of infra-red activity would become more and more nearly comparable with the dimensions of the electronic clouds more closely associated with the Na and the Cl nuclei. It would clearly, in these circumstances, cease to be justifiable to assume that the classical theory of small vibrations and its consequences would correspond with the facts of experiment. In other words, the appearance of overtones of the normal frequencies in absorption and the diminishing strength of such absorption with increasing frequency are both associated with the increasing amplitude of the resulting vibrations and the consequences arising therefrom.

We have already noticed that the normal mode of highest frequency would exhibit infra-red activity with great strength. It follows that this mode would also exhibit infra-red absorption of the higher orders in a conspicuous manner. It is also evident that the absence of infra-red activity of the four other modes of coupled oscillation which was remarked upon earlier would not extend to absorption of the higher orders corresponding to frequencies which are multiples of the frequencies of free vibration in those modes. For, their inactivity in the first order absorption was ascribed to the opposition of the phase of the oscillation in the alternate layers of the structure in those modes. When the amplitudes are large, the displacements of charge in one layer and in the next layer where the phase of the motion is opposite would not be numerically of equal magnitude and hence when they are summed up they would not cancel out completely. The residue would have twice the frequency of the oscillation. The octaves of these modes could therefore be expected to appear in absorption with considerable strength.

Another important consequence of the amplitudes of vibrations not being small is that the various normal modes would cease to be completely independent of each other. The sharpness of resonance which is a characteristic consequence of the theory of small vibrations would be notably departed from when, as in the present case, we have five normal modes which are spread over a wide range of frequencies and are not restricted to small amplitudes of vibration. In these circumstances, the energy of the incident radiation can be taken up for the excitation of vibrations which may be described as a superposition of two or more normal modes approximating to each other in frequency. It is also possible for a vibration to be excited which may be described as a superposition of one normal mode as a fundamental with another normal mode as an overtone with a frequency which is not very different. More generally, the radiation may excite vibrations which may



be described as a summation of two or more normal modes differing from each other in frequency and either as fundamentals or as overtones.

Earlier, we discussed the reflection of infra-red radiation which occurs when the incident radiation has the same frequency as the normal mode of highest frequency. We have now to remark that reflections of notable strength may also arise at other frequencies in consequence of the incident radiation exciting superposed vibrations of the kind referred to above with sufficiently large amplitudes. We shall have occasion to consider such cases later in this memoir.

### 5. THE ABSORPTION SPECTRA OF ROCK-SALT

Some excellent specimens of transparent salt were available in the museum of the Institute and it appeared worthwhile to study their behaviour in absorption, making use of the Leitz infra-red recording spectrophotometer with KBr optics which covers the spectral range between  $13\mu$  and  $24\mu$ . This, of course, is much outside the wavelength range within which powerful infra-red reflections are exhibited by rock-salt. The considerations set forth above however indicate that the absorption spectra of the higher orders could be recorded within the range of the instrument and evidence thus obtained both for the existence of such absorption and its relation to the specific modes and frequencies of vibration of the atomic nuclei in the crystal. Nine different thicknesses of the absorbing material ranging from 5.2 cm. down to 1.5 mm. were employed and their transmission percentages were recorded. A comparative study of the records reveals some very significant features. To illustrate them, the nine records are reproduced below in the text as Figs. 1 to 9, the absorption path being indicated below each figure.

Figure 1 recorded with a block 5.2 cm. thick exhibits nearly complete transparency at  $13\mu$ , followed by a progressive fall to opacity at  $18.5\mu$ , beyond which there is a complete cut-off of all transmission. Very similar features are also exhibited in Figs. 2 and 3 which were recorded with blocks which were respectively 4.3 and 2.8 cm. thick. It will be noticed, however, that a rapid improvement in transparency in the wavelength range between  $13\mu$  and  $14.5\mu$  appears as the absorption path is diminished. Whereas a difference of 18% in the transmissions at  $13\mu$  and  $14.5\mu$  is noticed in Fig. 1 for the block 5.2 cm. thick, the difference is only 12% in Fig. 2 for a thickness of 4.3 cm. and only 5% in Fig. 3 for a thickness of 2.8 cm. On the other hand, in the region of longer wavelengths, as will be seen on a comparison of Figs. 1, 2, 3, 4 and 5, there is little or no change in transmission produced by the large change in the absorption path from 5.2 to 1.5 cm.



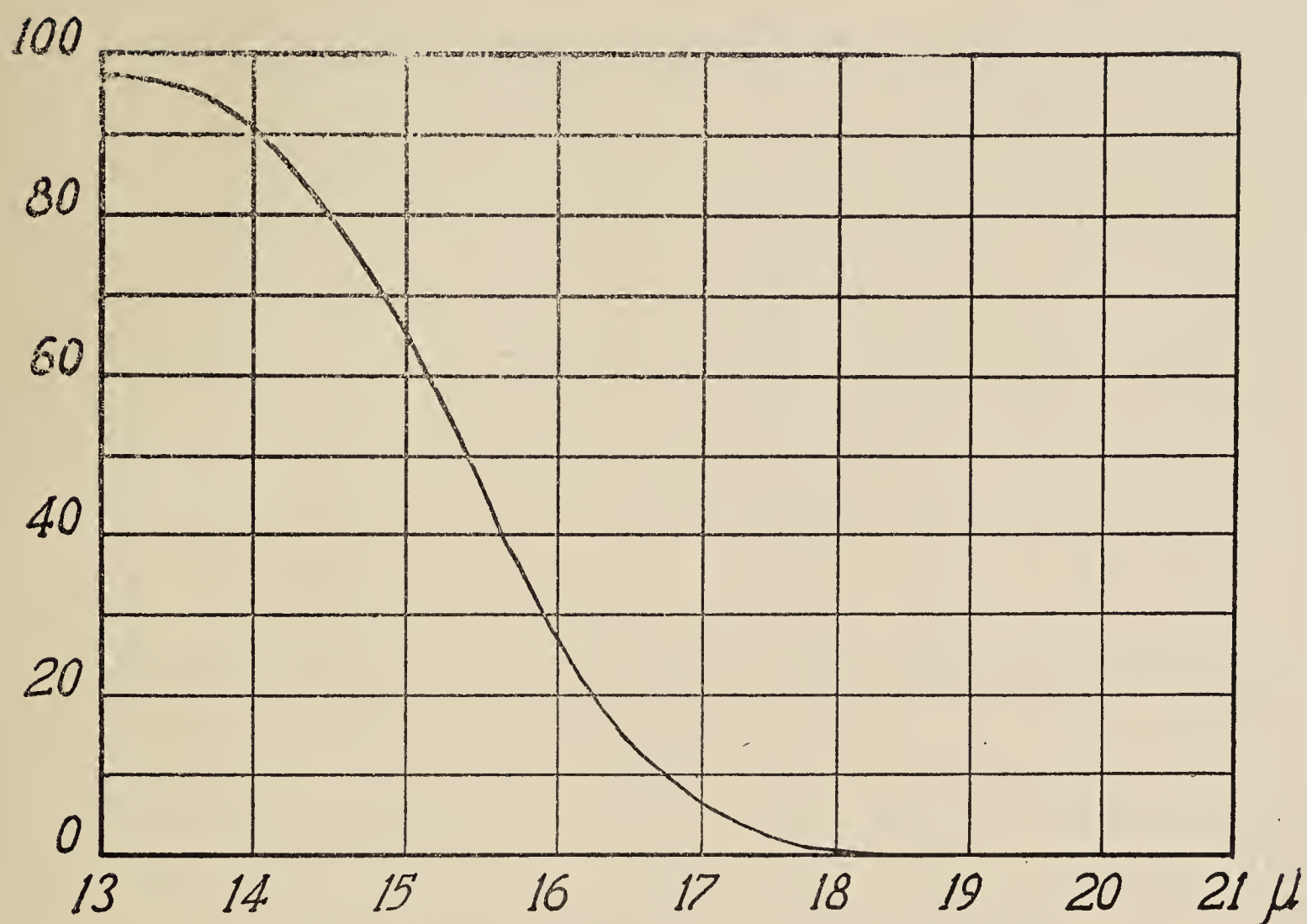


FIG. 1. Infra-Red Absorption by Rock-Salt : 5.2 cm.

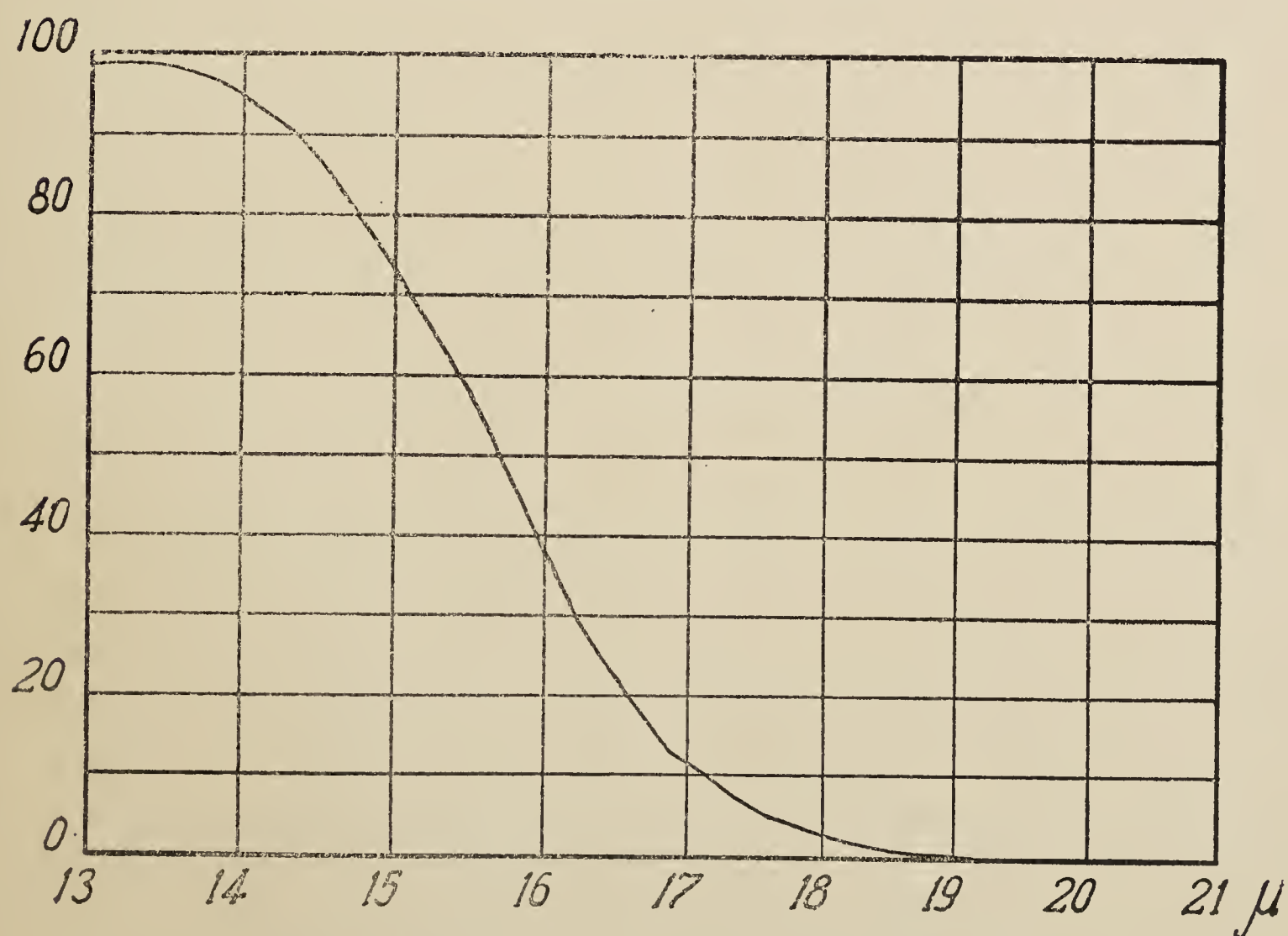


FIG. 2. Infra-Red Absorption by Rock-Salt : 4.3 cm.



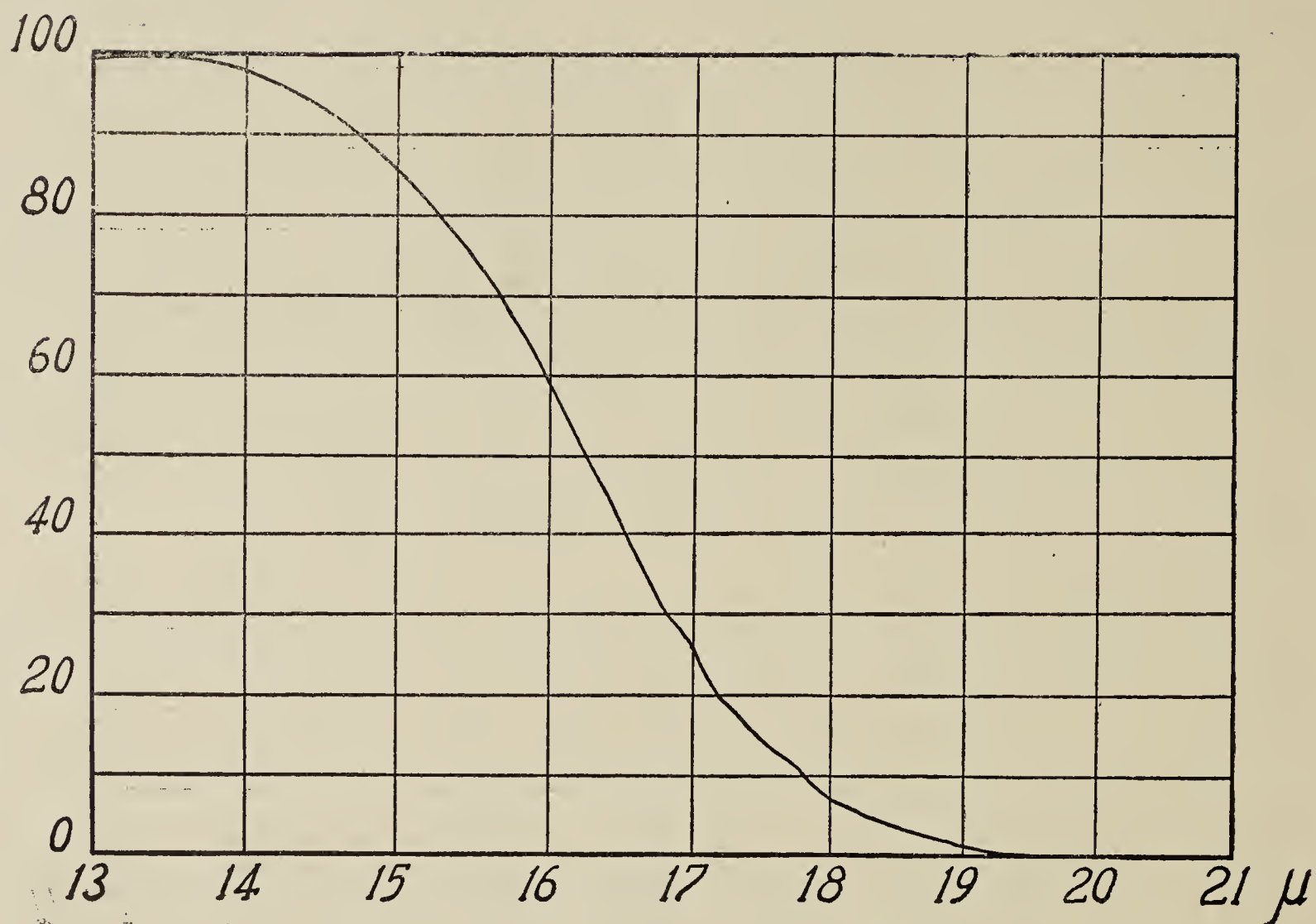


FIG. 3. Infra-Red Absorption by Rock-Salt : 2.8 cm.

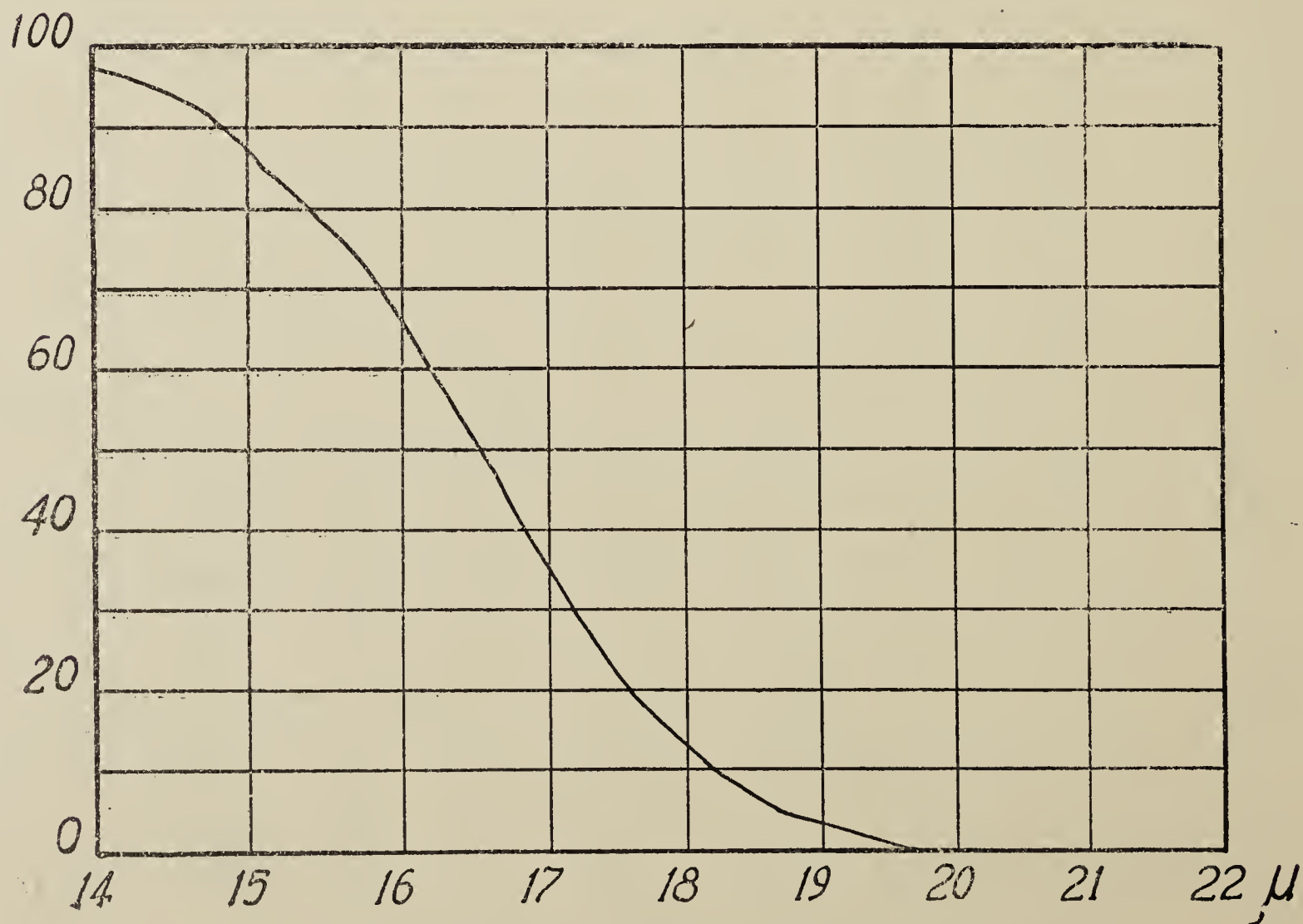


FIG. 4. Infra-Red Absorption by Rock-Salt : 2.1 cm.



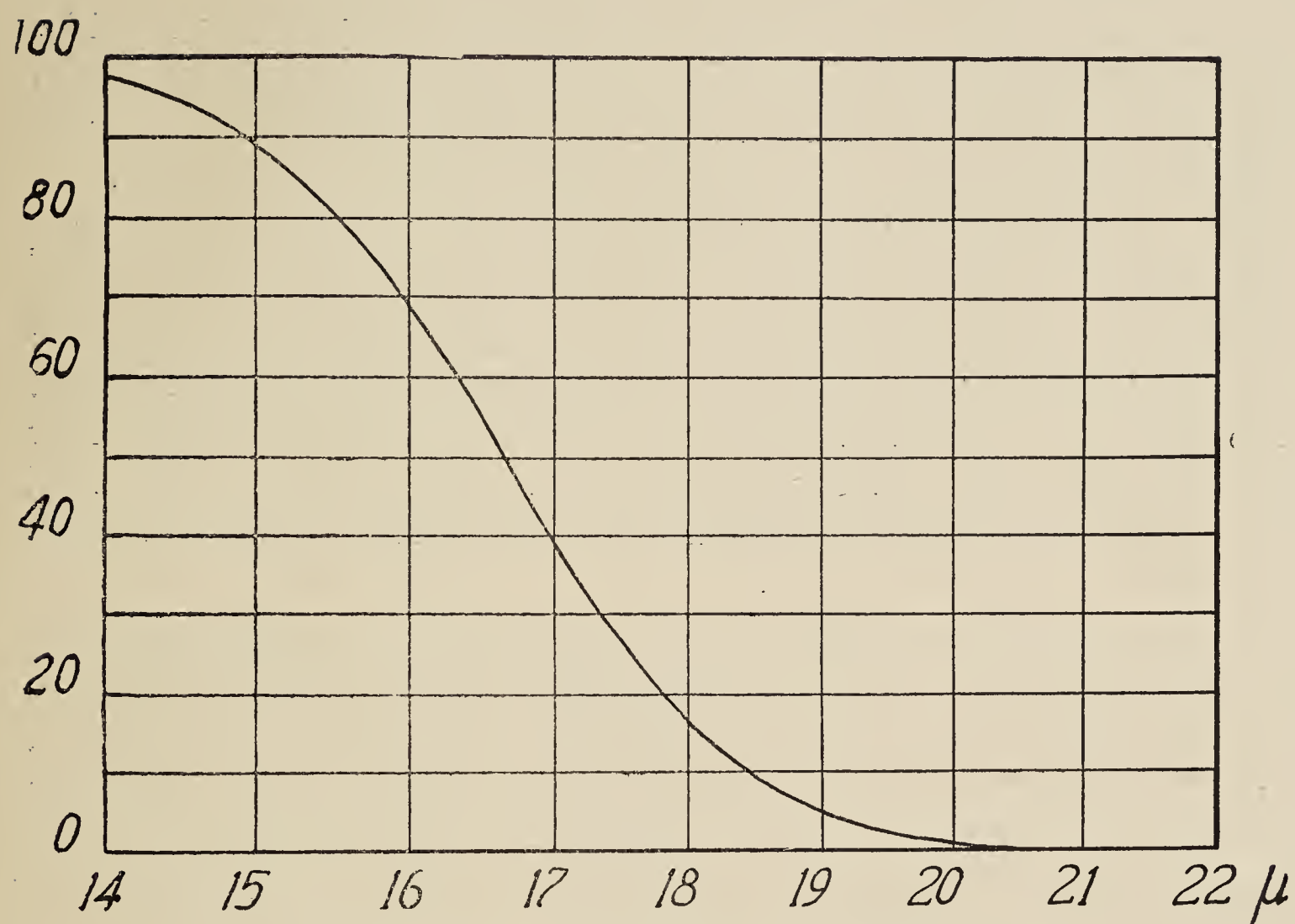


FIG. 5. Infra-Red Absorption by Rock-Salt : 1.5 cm.

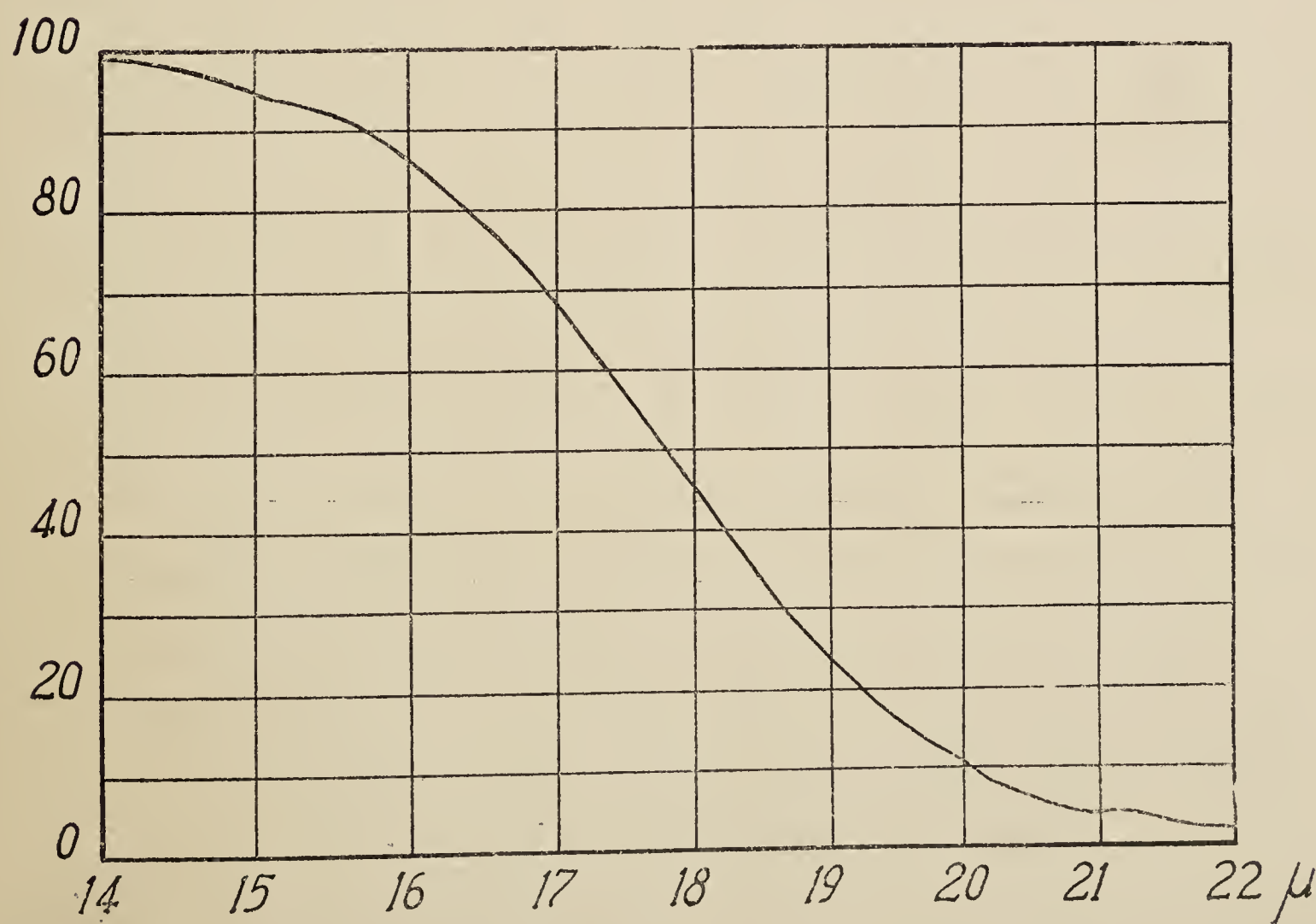


FIG. 6. Infra-Red Absorption by Rock-Salt : 0.8 cm.



The cut-off of the longer wavelengths persists and the transmission at  $19\mu$  is either zero or very small in all five cases. It is clear from the spectrographic records that the absorptions in the spectral regions from  $13\mu$  to  $19\mu$  and from  $19\mu$  to  $24\mu$  are of totally different orders of magnitude.

As is to be expected in the circumstances stated above, very striking changes appear in the form of the transmission curve when the thickness is greatly reduced and is of the order of a few millimetres only. Figures 6 to 9 are the records respectively for plates of thickness 8 mm., 4 mm., 2.5 mm. and 1.5 mm. The cut-off in the region of the longer wavelengths has now disappeared and is replaced by a transmission which increases from 25% at  $19\mu$  to 72% at the same wavelength as the thickness is diminished from 8 to 1.5 mm.

We may here draw attention to the remarkable fact that the percentage transmission curves are by no means always smooth graphs showing a progressive and continuous fall in transmission with increasing wavelength. Dips and sudden changes in direction are a noticeable feature. That they represent genuine features and not accidental faults in recording is shown by their appearance in the graphs for different thicknesses at the same wave-

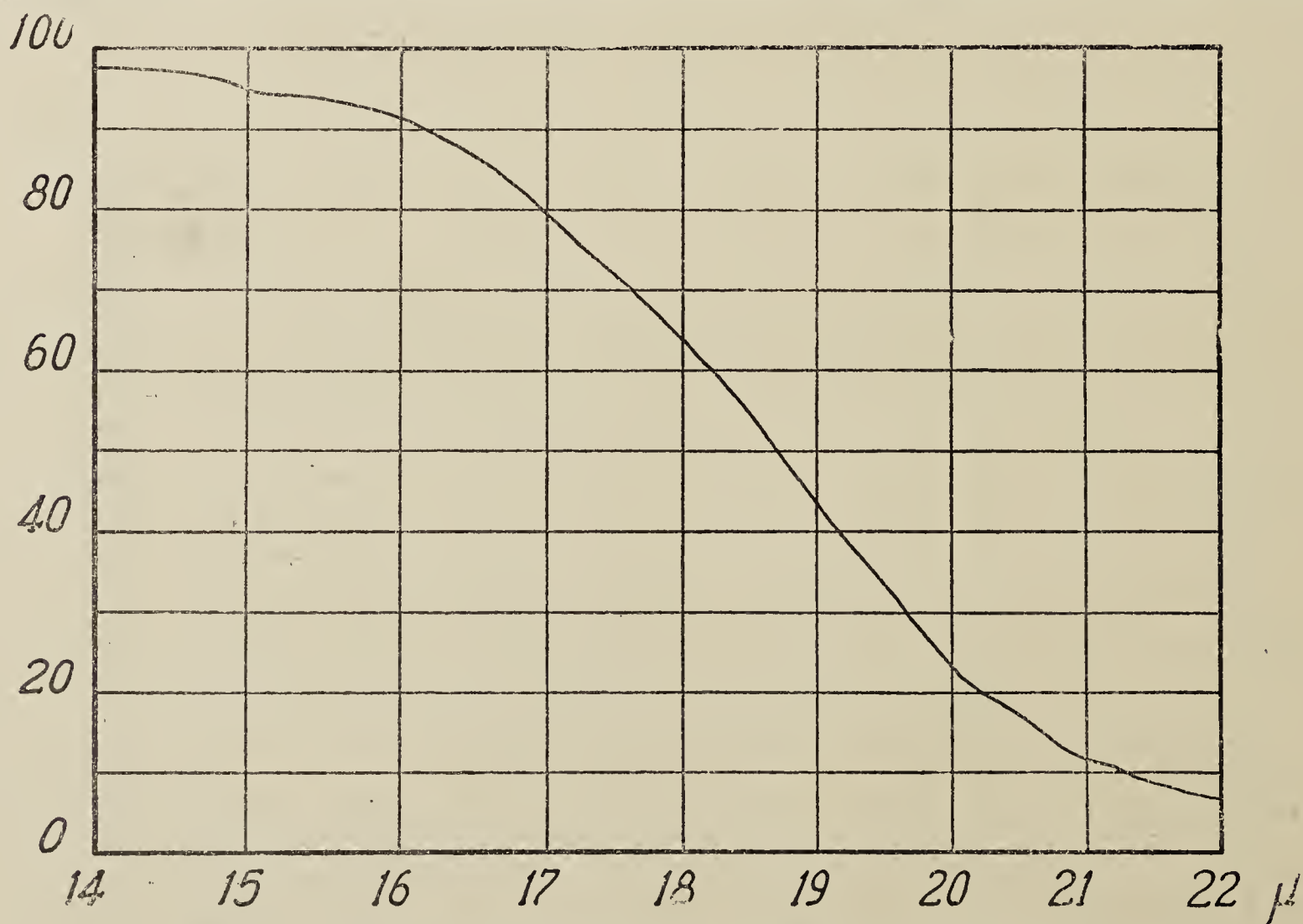


FIG. 7. Infra-Red Absorption by Rock-Salt : 0.4 cm.

lengths. It will suffice here to draw special attention to Fig. 8 which is the record for a plate 2.5 mm. thick. The curve as reproduced commences



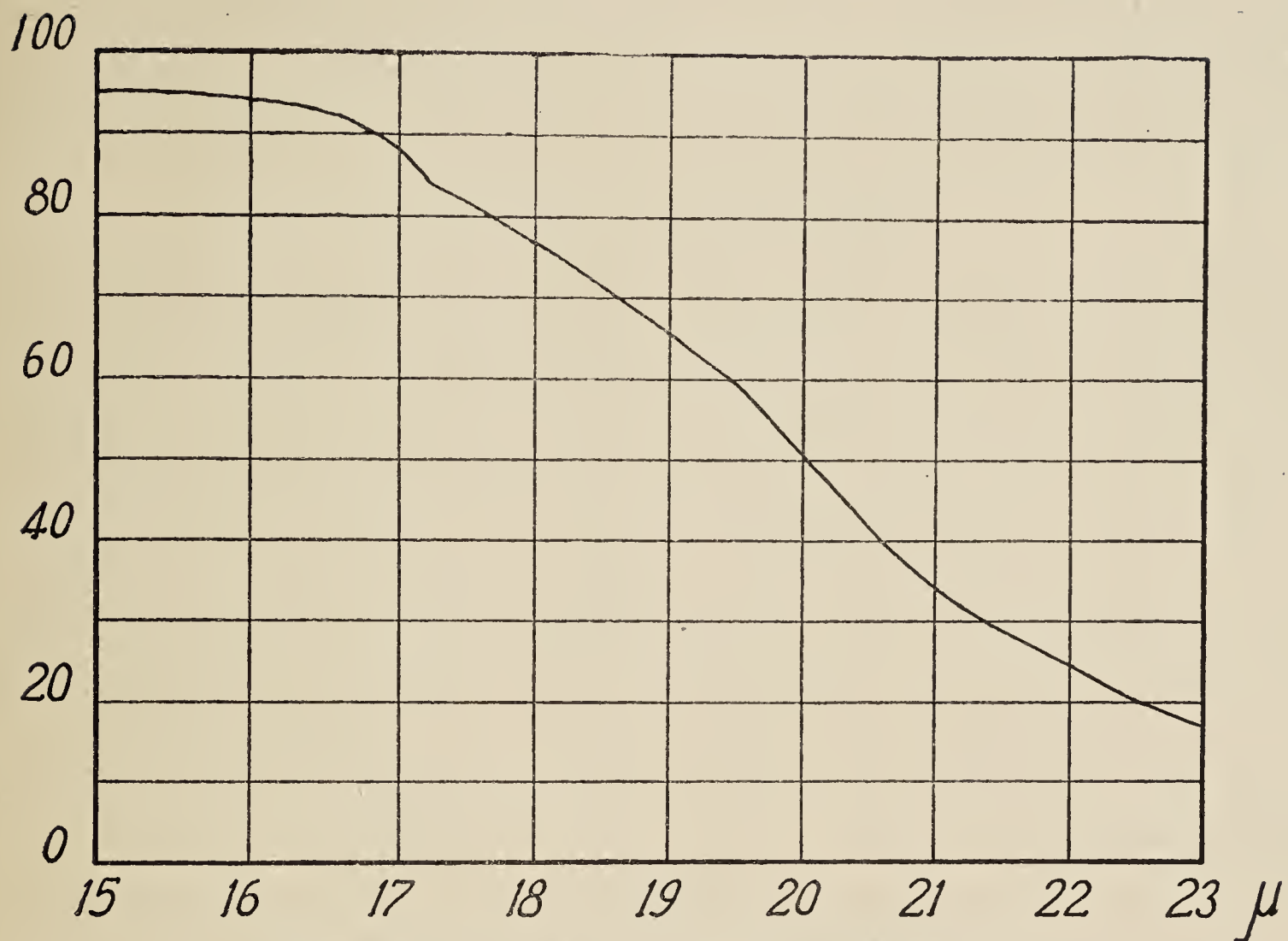


FIG. 8. Infra-Red Absorption by Rock-Salt : 0.25 cm.

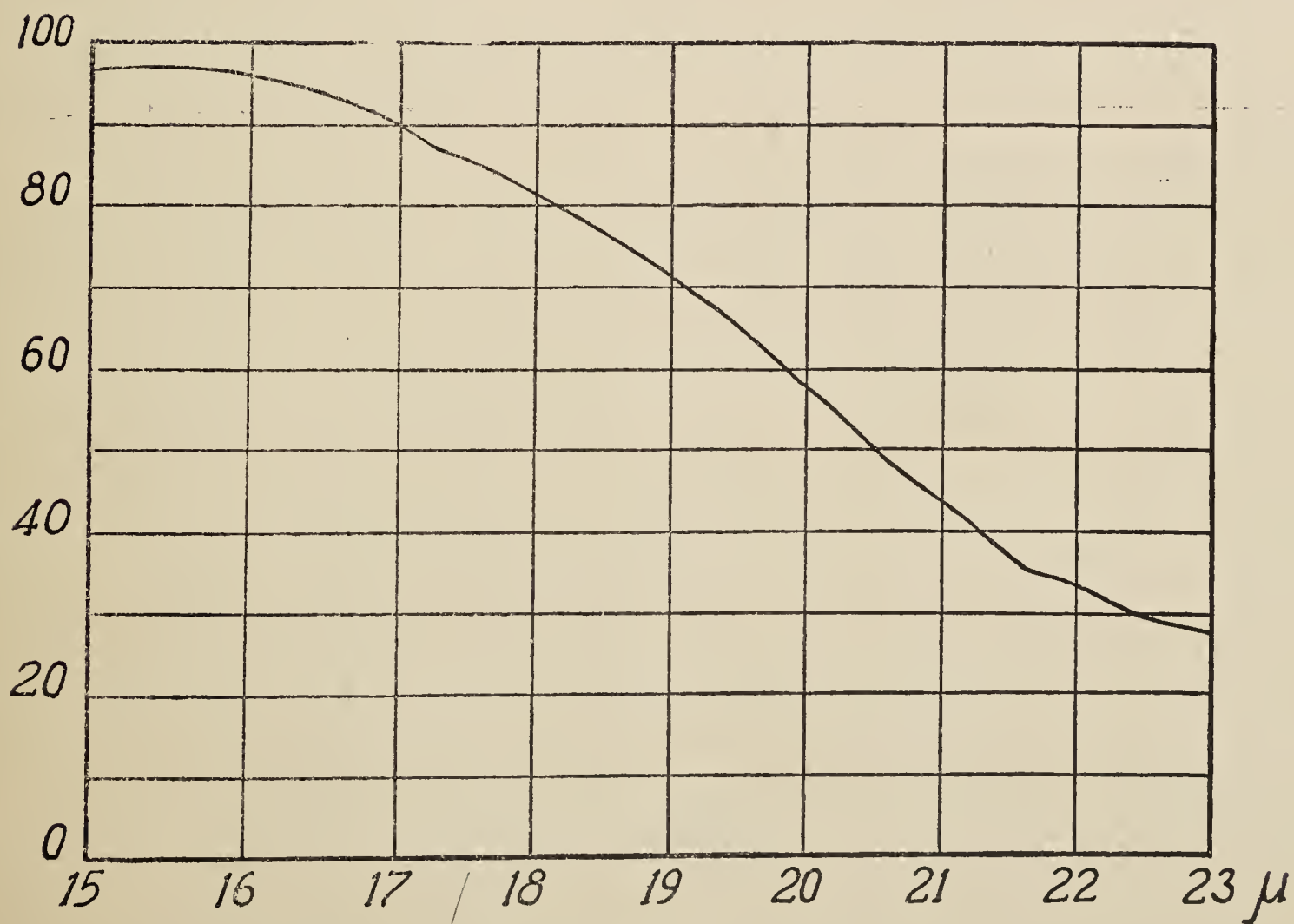


FIG. 9. Infra-Red Absorption by Rock-Salt : 0.15 cm.



with a 90% transmission at  $15\mu$ . This drops down rapidly and takes a sudden turn at  $17.2\mu$ . Another change in direction is noticeable at  $19.5\mu$ , still another at  $20.7\mu$  and finally a small but distinct change in direction at  $22\mu$ .

#### 6. SIGNIFICANCE OF THE RESULTS

We shall now proceed to show that the experimental results set forth above and also the results of the published studies of Barnes and Czerny, and of Mentzel cited in the first part of this memoir find an intelligible explanation in the light of the theoretical considerations expounded earlier in this memoir. We shall commence by assuming that the frequencies of the five modes of coupled oscillation of the Na and the Cl nuclei in rock-salt at room temperature are as shown below in Table I, both as wavelengths and as wave-numbers. The figures find their justification in the theoretical calculations presented in the first part of the memoir and corrected on the basis of the spectrographic data emerging from Rasetti's investigation. Table I also shows the overtones of the five frequencies up to and inclusive of the fifth order.

TABLE I  
*Vibration frequencies of rock-salt*

Mode	I Order	II Order	III Order	IV Order	V Order
I $\text{cm.}^{-1}$ ..	180	360	540	720	900
$\mu$ ..	55.6	27.8	18.5	13.9	11.1
II (a) $\text{cm.}^{-1}$ ..	150	300	450	600	750
$\mu$ ..	66.7	33.3	22.2	16.7	13.3
II (b) $\text{cm.}^{-1}$ ..	129	258	387	516	645
$\mu$ ..	77.5	38.8	25.8	19.4	15.5
II (c) $\text{cm.}^{-1}$ ..	110	220	330	440	550
$\mu$ ..	90.9	45.5	30.3	22.7	17.9
II (d) $\text{cm.}^{-1}$ ..	92	184	276	368	460
$\mu$ ..	109	54.5	36.2	27.2	21.7



A scrutiny of the figures in Table I enables us to understand the absorptive behaviour of rock-salt in the various ranges of frequency. In the wavelength range between  $13\mu$  and  $18\mu$ , the absorptions that could manifest themselves are the fourth-order absorptions of modes I and II (*a*) and the fifth-order absorptions of modes II (*a*), II (*b*) and II (*c*). These would necessarily be very weak and would need large absorption paths to enable them to be observed. They would also disappear quickly when the path is diminished. In the wavelength range between  $18\mu$  and  $24\mu$  the third-order absorptions of modes I and II (*a*) would appear, supplemented by the fourth-order absorptions of modes II (*b*) and II (*c*) and the fifth-order absorptions of mode II (*d*). The strength of the third-order absorptions would naturally be far greater than of those of higher orders appearing between  $13\mu$  and  $18\mu$ . It is, therefore, not surprising that thicknesses which allow a notable transmission in that region are completely opaque to greater wavelengths.

The vibrations of the structure responsible for the absorptions of the third, fourth and fifth orders would necessarily be of large amplitude. In consequence, the vibrations excited would be a superposition of the various normal modes approximating to each other in frequency and not the individual modes by themselves. In these circumstances, we could scarcely expect to find any observable evidence of the discreteness of the normal modes. Nonetheless, some indications of it do appear. The remarkable features noticed in the absorption curve reproduced in Fig. 8 for a thickness of 2.5 mm. may be cited as an example.

The absorptions of the second order would be far more powerful than those of the third order. Hence, much thinner layers, of the order of a hundred microns or less, would be needed to obtain any observable transmission in the region where the second-order absorptions operate. There is however much less crowding up of the normal modes. Hence it should be possible to find observational evidence of the discreteness of the absorption frequencies. The arrest in the absorption curve at about  $34\mu$  noticed by Mentzel with rock-salt plates some 30 microns thick is clearly identifiable with the second-order absorption of mode II (*a*) listed in Table I. Likewise, the arrest extending from  $40\mu$  to  $44\mu$  and observed with plates 8 microns thick by Barnes and Czerny is clearly a superposition of the second-order absorptions of modes II (*b*) and II (*c*) shown in Table I.

Using evaporated films of NaCl only a few microns thick, Barnes and Czerny succeeded in obtaining an observable transmission in the spectral region where the infra-red activity is strongest and intense reflections appear. They studied the spectral character of the transmitted radiation for various



thicknesses of the films employed by them. The results which they reported, as also Czerny's observations on the variations of the reflecting power with wavelength, form a study in themselves. They are more appropriately discussed in a later part of this memoir.

#### SUMMARY

Infra-red activity is shown to be a consequence of the periodic movements of the electron clouds in the crystal excited by the field of the incident radiation. The accompanying oscillations of the positively charged nuclei determine the frequencies but are not themselves the cause of the activity.

It is shown that of the nine modes of free vibration of the rock-salt structure, the mode of highest frequency is intensely active both in the first and the higher orders. Four other modes are inactive in the first order but active in higher orders. The remaining four are totally inactive. Spectrographic records of the absorption of rock-salt over a wide range of thicknesses are presented and explained in terms of the activity of these modes. The results reported by Mentzel and by Barnes and Czerny on the transmission spectra of rock-salt are explained on the same basis.



# THE SPECTROSCOPIC BEHAVIOUR OF ROCK-SALT AND THE EVALUATION OF ITS SPECIFIC HEAT

## Part III. The Spectrum of Light Scattering

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### 1. INTRODUCTION

IN the first part of this memoir, the modes of free vibration characteristic of the structure of rock-salt were described and it was shown how their frequencies could be computed. In the second part of the memoir, the activities of these modes in the absorption and reflection of infra-red radiation were discussed. Experimental data were presented which showed clearly that the normal mode of highest frequency is active not only as a fundamental but also as overtones of higher orders. The observed infra-red behaviour of rock-salt over a wide range of frequencies of the incident radiation was discussed and explained in terms of the activities of its characteristic modes of vibration.

The present part of the memoir is concerned with an entirely different spectroscopic technique which enables the existence of the discrete normal modes of vibration to be established and their frequencies as theoretically evaluated to be checked by comparison with the results of experiment. This technique makes use of the frequency shifts observed when monochromatic light traversing the crystal emerges after diffusion in its interior and the diffused radiation is examined spectroscopically. The intensity of the radiation so diffused is a very small fraction of that traversing the crystal. But this very circumstance makes the procedure one of the highest value for the purposes in view. For, the complications which are inherent in the use of infra-red radiation in the study of the spectroscopic behaviour of such an intensely absorbing material as rock-salt are entirely avoided. The spectroscopic picture of the crystal which emerges from the recorded spectra of the diffused light is very simple, clear and definite.

We shall begin with a few remarks of a general nature. The study of the diffusion of monochromatic light by the molecules of diatomic gases,



*e.g.*, oxygen and nitrogen, gives us an insight into the origin of the frequency shifts in light-scattering. These shifts are readily identifiable with the characteristic vibrational frequencies of the molecules. The appearance of scattered radiations of altered wavelength is thus explicable as a consequence of a periodic variation in the power of the molecule to scatter light resulting from the relative movements of its atoms in such vibration. A similar explanation can be given for the frequency shifts observed in the diffusion of light by crystals, the structural units in the crystal instead of the molecules of the gas being regarded as the vibrating systems. The structural units in a crystal are held to fixed positions and cannot move freely in the manner of the molecules in a gas. This circumstance has necessarily to be taken into account in considering the dynamics of their vibrations. But in respect of the frequency shifts arising from their internal vibrations, the randomness of phase of the scattered radiations renders the situation not essentially different from that of scattering by the individual molecules of a gas.

## 2. SCATTERING OF LIGHT WITH DOUBLED FREQUENCY SHIFTS

As has been remarked above, the frequency shifts observed in the scattering of light may usually be identified with the vibrational frequencies of the scattering units. There is however a remarkable class of cases in which spectral shifts are observed having double the frequency of the vibrational modes which give rise to them. We may as an illustration mention the facts emerging from a study of the scattering of light in calcite. The  $\text{CO}_3$  groups in that crystal have four internal modes of vibration. Three of them give frequency shifts of  $712\text{ cm.}^{-1}$ ,  $1086\text{ cm.}^{-1}$  and  $1436\text{ cm.}^{-1}$  which may be identified respectively with the frequencies of three possible modes of vibration of the  $\text{CO}_3$  group in its own plane. We are here concerned with a fourth frequency shift of  $1749\text{ cm.}^{-1}$  which is recorded with an intensity about equal to that of the  $1436\text{ cm.}^{-1}$  shift.

Now, the fourth mode of vibration of the  $\text{CO}_3$  group is an out-of-plane movement in which the C atom oscillates along a line perpendicular to the  $\text{O}_3$  group and finds itself alternately above and below the plane of the group. Such an oscillation may be expected to be strongly active in the absorption of infra-red radiation. Actually, a well-defined peak appears in the infra-red absorption spectrum of calcite at about  $874\text{ cm.}^{-1}$  and this is identified as arising from just such a vibration. But no line having that frequency shift or anywhere near it is recorded in the spectrum of the scattered light. We are thus obliged to infer that the frequency shift of  $1749\text{ cm.}^{-1}$  arises from



the infra-red active vibrational mode but is recorded in the scattering of light with double its frequency.

A doubling of the frequency shift in light-scattering as compared with an infra-red absorption frequency may be explained in the following manner. The infra-red activity arises from the movements of the electron clouds in the crystal. These movements have necessarily the same frequency as the movements of the atomic nuclei. In the scattering of light, however, we are concerned with the optical polarisability of the entire electronic cloud and this depends on its geometric configuration. In the particular case of the  $\text{CO}_3$  group in calcite it is clear that the configuration of the group takes the same form twice in each oscillation. The periodic variation of optical polarisability has therefore twice the frequency of the vibration and hence the resulting frequency shift is also doubled. What is specially remarkable is that its intensity is comparable with those of the frequency shifts of the ordinary kind due to the other modes of vibration and that it is far greater than the intensity with which a shift of  $2173 \text{ cm.}^{-1}$  (double that of the planar oscillation of  $1086 \text{ cm.}^{-1}$ ) is recorded in the spectrum.

### 3. THE ROCK-SALT SPECTRUM

We proceed to show that an effect of the same general nature as that considered and explained above in the case of calcite is exhibited by all the nine normal modes of vibration of the rock-salt structure. We may begin by considering the triply degenerate mode of highest frequency which is highly active in the absorption of infra-red radiation. In this mode the sodium and chlorine nuclei with their associated electronic clouds move in opposite phases with amplitudes inversely proportional to their masses. *Twice* in each oscillation, a chlorine nucleus comes closest to a sodium nucleus either from one side or from the other. In such an approach, the power of the NaCl group to scatter light is notably increased beyond what it is when the Na and Cl nuclei are separated by their normal spacing in the crystal. Accordingly, the periodic variations of the scattering power of the NaCl groups in the crystal have *twice* the frequency of the vibrational mode. The frequency shift to which it gives rise is therefore also of double frequency. A component having the same frequency as the vibrational mode is totally absent, since the approach of a chlorine nucleus to a sodium nucleus is balanced by the recession of a chlorine nucleus from the same sodium nucleus on the opposite side. In other words, the vibrational mode is antisymmetric with respect to each sodium nucleus and each chlorine nucleus in the assembly. It is therefore inactive in light-scattering in the sense of the term as ordinarily understood.



The same argument may be extended to the four other coupled oscillations of the Na and Cl nuclei. Two of these modes are tangential and the two others normal to the cubic layers in the crystal; in all these cases, the movements in alternate layers are in opposite phases. In the tangential mode designated in the earlier parts of this memoir as II (*a*), the Na and Cl nuclei approach and recede from each other in much the same manner as in the mode I discussed above. The alternation in phase from layer to layer leaves the argument unaffected; for, at the instant when the Cl and Na nuclei are closest to each other in one layer, they would also be closest to each other in the next layer. It follows that mode II (*a*) would be active in the double-frequency modified scattering of light to much the same extent as the principal mode already considered. Indeed, mode II (*a*) having a degeneracy of six may be expected to exhibit a greater intensity than mode I which is only triply degenerate.

Considering next the tangential mode designated as II (*d*) in which the Na and Cl nuclei in each cubic layer oscillate in the same phase, the phases of the movements being reversed in the successive layers, it is evident that the double-frequency effect would also arise in respect of this mode but it would be very much feebler. For, the movements of the Na and the Cl nuclei being in the same phase, their approaches to each other would necessarily be much less close than when the movements are in opposite phases. The periodic fluctuations in the scattering power of the NaCl groups would therefore be relatively small and hence the observable effect of mode II (*d*) as recorded in the spectra of the scattered light should be far less conspicuous.

Arguments of the same kind may be extended to the consideration of the activity of the triply degenerate oscillations of the Na and Cl nuclei normal to the cubic planes designated as modes II (*b*) and II (*c*) respectively. In mode II (*b*) the Na and Cl nuclei move in the same phase and this has the higher frequency, while II (*c*) in which they move in opposite phases has the lower frequency. But the approaches between the Cl and Na nuclei which give rise to an increased scattering power are those between the nuclei which are in adjacent layers. Hence, it follows that the mode II (*b*) of the higher frequency would be much more strongly active than mode II (*c*) of the lower frequency. Since both the modes are only three-fold degenerate, their recorded intensities would be low. In particular, the mode II (*c*) of lower frequency would be recorded only very feebly.

#### 4. ACTIVITY OF THE OCTAHEDRAL MODES

We now proceed to discuss the activity of the modes in which the Na nuclei alone, or the Cl nuclei alone oscillate. The layers containing them



are the octahedral planes of the crystal and the movement is either perpendicular or parallel to those planes, its phase being reversed in the successive layers. The oscillations perpendicular to the octahedral planes have a degeneracy of four and the nuclei move along the body-diagonals of the cube. The oscillations tangential to those planes have a degeneracy of eight and the nuclei move along one or another of the two-face diagonals appearing in the octahedral planes.

We proceed to consider the nature of the movements in these modes. In the perpendicular modes, a nucleus would approach its three nearest neighbours on the one side and recede from its three nearest neighbours on the other side. In the parallel modes, a nucleus would approach two of its nearest neighbours on one side and recede from two of its nearest neighbours on the other side. In either case, the movements would not give rise to frequency-shifts in light-scattering of the usual kind. They would, however, all be active in the modified scattering of double frequency. The parallel movements, being twice as numerous, may be expected to be recorded with greater intensity than the perpendicular ones.

We may summarise the overall picture which emerges from the foregoing considerations regarding the spectroscopic behaviour of rock-salt in light-scattering as follows:

- (a) All the nine normal modes would exhibit a doubled frequency shift but with very different intensities.
- (b) The triply degenerate mode of highest frequency would be strongly recorded but would be inferior in intensity to the cubic mode of lower frequency similar to it in character but which is six-fold degenerate.
- (c) The two cubic modes of low frequency would be recorded only feebly, the one which is three-fold degenerate even more weakly than the other of lowest frequency which is six-fold degenerate.
- (d) The eight-fold degenerate oscillation of the chlorine nuclei tangential to the octahedral planes should appear with notable intensity as a conspicuous feature in the spectrum, being adjacent to the two feebly recorded modes of lowest frequency.
- (e) The eight-fold degenerate oscillation of the sodium nuclei parallel to the octahedral planes would be recorded more strongly than the four-fold degenerate movement perpendicular to those planes.



## 5. THE SPECTRUM OF LIGHT SCATTERING

The vibration frequencies of the five cubic modes involving coupled oscillations of the Na and the Cl nuclei were listed in an earlier part of this memoir. To this list we must now add the frequencies of the four octahedral modes in which only the Na or only the Cl nuclei oscillate. As a rough approximation, the frequencies of these modes can be expressed in terms of the infra-red active mode of highest frequency by replacing the reduced mass of the two nuclei in its formula by the mass of the Na nucleus alone or of the Cl nucleus alone. But, as already remarked upon and explained in the first part of the memoir, the values thus obtained need correction and their frequencies have to be increased by amounts which are greater for the perpendicular vibrations than for the parallel ones. The corrected frequencies are most conveniently determined from the spectral shifts observed in light scattering, as they are readily identified in those spectra.

TABLE I  
*Modes and frequencies (cm.<sup>-1</sup>)*

Modes	De- gene- racy	Princi- pal mode	Cubic class	Octa- hedral class	Doubled fre- quency	Intensity
I	3	180 (NaCl)	..	..	360	Moderate
III (a)	4	..	..	170 (Na)	340	Moderate
III (b)	8	..	..	157 (Na)	314	Strong
II (a)	6	..	150 (NaCl)	..	300	Strong
III (c)	4	..	..	140 (Cl)	280	Strong
II (b)	3	..	129 (NaCl)	..	258	Weak
III (d)	8	..	..	117.5 (Cl)	235	Intense
II (c)	3	..	110 (NaCl)	..	220	Very weak
II (d)	6	..	92 (NaCl)	..	184	Weak

Table I gives the frequencies of all the nine normal modes. Their degeneracies and descriptions are also shown. They have been entered in Table I in the descending order of frequency. The doubled frequency



shifts in light scattering appear in the penultimate column. The entry against each frequency shift under the head intensity is based on the indications of theory, *viz.*, the degeneracy of the mode and the nature of the movements involved. These considerations have already been discussed in detail above and need not therefore be repeated here.

## 6. THE CONSEQUENCES OF THERMAL AGITATION

It is a familiar experience in studies on the scattering of light in crystals to find that the observed frequency shifts exhibit a thermal effect. The lines sharpen and the frequency shifts show a readily measurable increase when the crystal is cooled down to liquid air temperature. When, on the other hand, the crystal is warmed up, the lines become more diffuse as the result of an asymmetrical broadening. As a consequence of such broadening, the frequency shifts also diminish. The effects of this nature are both absolutely and relatively more conspicuous in the case of the vibrational modes of low frequencies. As examples may be mentioned the behaviour of calcite and of quartz in which they have been very fully studied. A thermal broadening and the accompanying diminution of the frequency shifts would necessarily occur also in the case of rock-salt. Since we are concerned with double-frequency scattering, they would be magnified two-fold. On the basis of the known data for quartz and calcite we may expect a broadening of the lines in the spectrum of rock-salt of about ten wave-numbers.

It follows from what has been stated that in the crowded spectrum indicated by the figures in Table I, the thermal broadening would result in the resolution of the frequency-shifts which are not very different becoming distinctly imperfect. When, however, a strongly recorded frequency shift has only weak companions on either side, its character as a discrete line-shift would be more clearly apparent.

## 7. COMPARISON WITH THE EXPERIMENTAL RESULTS

With a crystal of rock-salt five centimetres thick which was illuminated by the extremely intense ultra-violet radiation at  $\lambda$  2536.5 emitted by a water-cooled magnet-controlled mercury arc in quartz and giving an exposure of 8 hours, Rasetti obtained a remarkable spectrogram. This was published with a microphotometer record of the spectrum alongside of it. An enlargement of this microphotometer curve copied directly from Rasetti's original publication is reproduced below as Fig. 1 in the text.

A special method was employed by Rasetti to prevent the complete fogging of the photographic plate which would have otherwise resulted from





FIG. 1. Microphotometer Record (after Rasetti).

such prolonged exposure to intense illumination. A filter of mercury vapour was introduced which absorbed the  $2536\cdot5$  radiation entering the instrument before it reached the photographic plate. A remarkably clear and well-exposed spectrogram was thus obtained. Neither the accompanying  $\lambda$   $2535$  radiation nor the faint continuum extending to about 50 wave-numbers on either side of  $\lambda$   $2536\cdot5$  is cut out by the filter. They are recorded on the spectrogram, but have no significance.

The frequency shifts which arise from the scattering of the  $2536\cdot5$  radiation in rock-salt are all found to lie between the limits  $360\text{ cm.}^{-1}$  and  $184\text{ cm.}^{-1}$  indicated by the theory. Beyond these limits, the spectrum falls off steeply in intensity. The fall on both sides would have been even steeper had the inevitable background of continuous spectrum which is an accompaniment of the monochromatic radiations of the mercury arc been totally absent in the record. But such absence could scarcely have been hoped for in view of the prolonged exposures necessary to obtain the spectrum.



For the convenience of the reader, the original spectrogram of rock-salt has been reproduced in a somewhat enlarged form as Fig. 1 in Plate VII accompanying the present memoir. On an inspection of the spectrum, it is evident that it presents precisely those features which would result from the nine double-frequency shifts listed in Table I being recorded in the positions and with the relative intensities listed in Table I. On closer examination, it becomes clear that the correspondence between the observed spectrum and the theoretical conclusions listed in Table I extends to all the observable details in it. The experimental conditions, *viz.*, the small dispersion of the spectrograph and the broadening of the frequency-shifts by the thermal agitation in the crystal are unfavourable to a complete resolution of the nine frequency shifts from each other. Nevertheless, it is clear that they are all present and have the positions and relative intensities indicated by the theory.

We may begin by referring to a striking feature in the spectrogram, *viz.*, the well-defined frequency shift of  $235\text{ cm.}^{-1}$  which stands out in the record on both sides of the exciting radiation. The shift appears in a part of the spectrum where the frequency shifts on either side are weak or very weak as indicated by the theory and also as actually observed. Naturally, therefore, the  $235\text{ cm.}^{-1}$  frequency shift is permitted to exhibit its true character as a discrete line-shift. It is not surprising also that the intensity of the shift due to the eight-fold degeneracy of the vibration makes it a prominent feature in the spectrum.

The two lowest frequencies listed in Table I are coupled oscillations of the Na and the Cl nuclei appearing in the cubic planes. The theory indicates that they would appear in the spectrum with a much lower order of intensity than the other modes, the reason being the Na and Cl nuclei have the same phase of vibration and cannot therefore make close approaches to each other. The two modes should also differ in their relative intensities by reason of the degeneracies being different, being three and six respectively. These consequences of the theory are in striking accord with the experimental facts. Actually, the frequency shifts of  $220\text{ cm.}^{-1}$  and  $184\text{ cm.}^{-1}$  are by far the feeblest recorded in the spectrum. The shift of  $220\text{ cm.}^{-1}$  is, in particular, so weak as scarcely to be visible in the reproduction of the spectrum. Its presence in the microphotometer record can be made out with some difficulty being obscured by the steep rise in the intensity as we approach the intense  $235\text{ cm.}^{-1}$  shift. The shift of  $220\text{ cm.}^{-1}$  can, however, be readily recognised in the microphotometer record on the “anti-stokes” side of the spectrum as a second and weaker hump between the  $184\text{ cm.}^{-1}$  and  $235\text{ cm.}^{-1}$  shifts. (Figure 1 in the text, right-hand side of the microphotometer curve.)



It is a significant consequence of the theory that the smaller frequency shift of  $300\text{ cm.}^{-1}$  should be recorded with twice the intensity of the larger shift of  $360\text{ cm.}^{-1}$  by reason of its higher degeneracy, though the oscillations are very similar to each other in character. That this is actually the case is clear from the spectrogram itself. In the microphotometer record (Fig. 1 in the text, left-hand side of the curve), the frequency shift of  $300\text{ cm.}^{-1}$  stands at a much higher level than  $360\text{ cm.}^{-1}$ . It is well known, however, that differences in intensity between the different lines in a spectrogram are better appreciated when the exposure is not very heavy, as the photographic blackening is then not too great to show up the gradations in exposure. Likewise, for a microphotometer record, a moderately exposed plate is more suitable than a heavily exposed one. For, in the latter case, the differences of intensity are greater reduced in the transmission through the blackened plate which is recorded photometrically.

The importance of the foregoing remarks will be realised on an examination of the microphotometer record reproduced above in the text as Fig. 1. Rasetti's spectrogram and its microphotometer trace show the spectral shifts recorded on both sides of the exciting radiation  $\lambda 2536.5$ . On the "anti-stokes" side, the exposures are much less heavy and hence its microphotometric record is better suited to exhibit the relations of intensity between adjacent parts of the spectrum than the record of the more heavily exposed spectrum on the other side.

It has been already remarked that the  $220\text{ cm.}^{-1}$  shift which is only vaguely indicated on the heavily exposed side of the record is quite clearly seen on the "anti-stokes" side. Likewise, all the frequency shifts listed in Table I are clearly visible on the "anti-stokes" side of the microphotometer record distinctly separated from each other. Instead of the  $360\text{ cm.}^{-1}$  and  $340\text{ cm.}^{-1}$  shifts appearing fused into a single band as on the heavily exposed side, they are seen on the "anti-stokes" side quite clearly as two distinct steps one above the other. The third step which is visible in the record is the  $314\text{ cm.}^{-1}$  shift. Two other strongly recorded shifts, *viz.*,  $300\text{ cm.}^{-1}$  and  $280\text{ cm.}^{-1}$ , are seen higher up in the photometer curve. The weak  $258\text{ cm.}^{-1}$  shift appears as the drop in intensity which immediately precedes the strongly recorded peak shift of  $235\text{ cm.}^{-1}$ . Thus, the microphotometer record on the "anti-stokes" side enables us to recognise all the nine frequency shifts individually and to appreciate the great differences in intensity which they present more clearly than the record on the heavily exposed side permits.

We may sum up the foregoing by stating that the experimental results completely establish the correctness of our theoretical approach and are a



verification of the various observable consequences to which the theory points.

## 8. SUMMARY

All the nine normal vibrational modes of the rock-salt structure can give frequency shifts in light-scattering which are twice their respective frequencies but are of very different intensities, determined by their degeneracies and the nature of the movements of the Na and Cl nuclei in those modes. The doubled frequencies in  $\text{cm.}^{-1}$  with their respective degeneracies are 360 (3), 340 (4), 314 (8), 300 (6), 280 (4), 258 (3), 235 (8), 220 (3), 184 (6). The spectroscopic facts are in full agreement with the theoretical deductions.



## APPENDIX

### REFLECTION AND TRANSMISSION OF LONG WAVES

The frequencies of the characteristic vibrational modes of the rock-salt structure determined spectroscopically and expressed as infra-red wavelengths are the following:  $55.6\ \mu$ ,  $58.8\ \mu$ ,  $63.7\ \mu$ ,  $66.7\ \mu$ ,  $71.4\ \mu$ ,  $77.5\ \mu$ ,  $85.0\ \mu$ ,  $90.9\ \mu$  and  $108\ \mu$ . The question arises of the part they play in the reflection by rock-salt surfaces and in the transmission through thin films of long-wave infra-red radiation.

Amongst these modes, that of the highest frequency with the characteristic wavelength  $55.6\ \mu$  stands in a class apart by itself, being the strongly infra-red active fundamental. It is therefore to be expected that this mode would play a dominating role in the reflection of infra-red radiation and that it would also manifest itself as the principal cause of absorption in thin films.

The reflecting power of rock-salt actually reaches its maximum value of about 90% at a wavelength which is nearly the same as that of its active fundamental. But it is considerable both at shorter and at longer wavelengths. On the long wavelength side, the reflecting power diminishes progressively and reaches a limiting value of 20% at and beyond  $100\ \mu$ . On the short wavelength side, the reflecting power drops off more quickly and becomes quite small at about  $33\ \mu$ . There are indications of a minor maximum of reflecting power at about  $38\ \mu$ .

That the reflecting power at shorter wavelengths is considerable is readily explained. Four of the characteristic vibrational modes are coupled oscillations of the Na and the Cl nuclei in the crystal which are strongly infra-red active with a *doubled frequency*. The absorption wavelengths thus arising are  $33.3\ \mu$ ,  $38.8\ \mu$ ,  $45.5\ \mu$  and  $54.3\ \mu$  respectively. The existence of absorptions at these wavelengths is indeed demonstrable by observations with rock-salt plates with appropriately chosen thicknesses. Their co-operation with the active fundamental in infra-red reflection is a natural consequence. That the reflecting power becomes negligible at wavelengths less than  $33\ \mu$  is only to be expected in these circumstances.

The existence of a whole series of normal modes of vibrations of the rock-salt structure with characteristic wavelengths ranging between  $55\ \mu$  and  $108\ \mu$  furnishes us with a clue to the explanation of the fact that the reflecting power of rock-salt diminishes only slowly in this range and reaches its



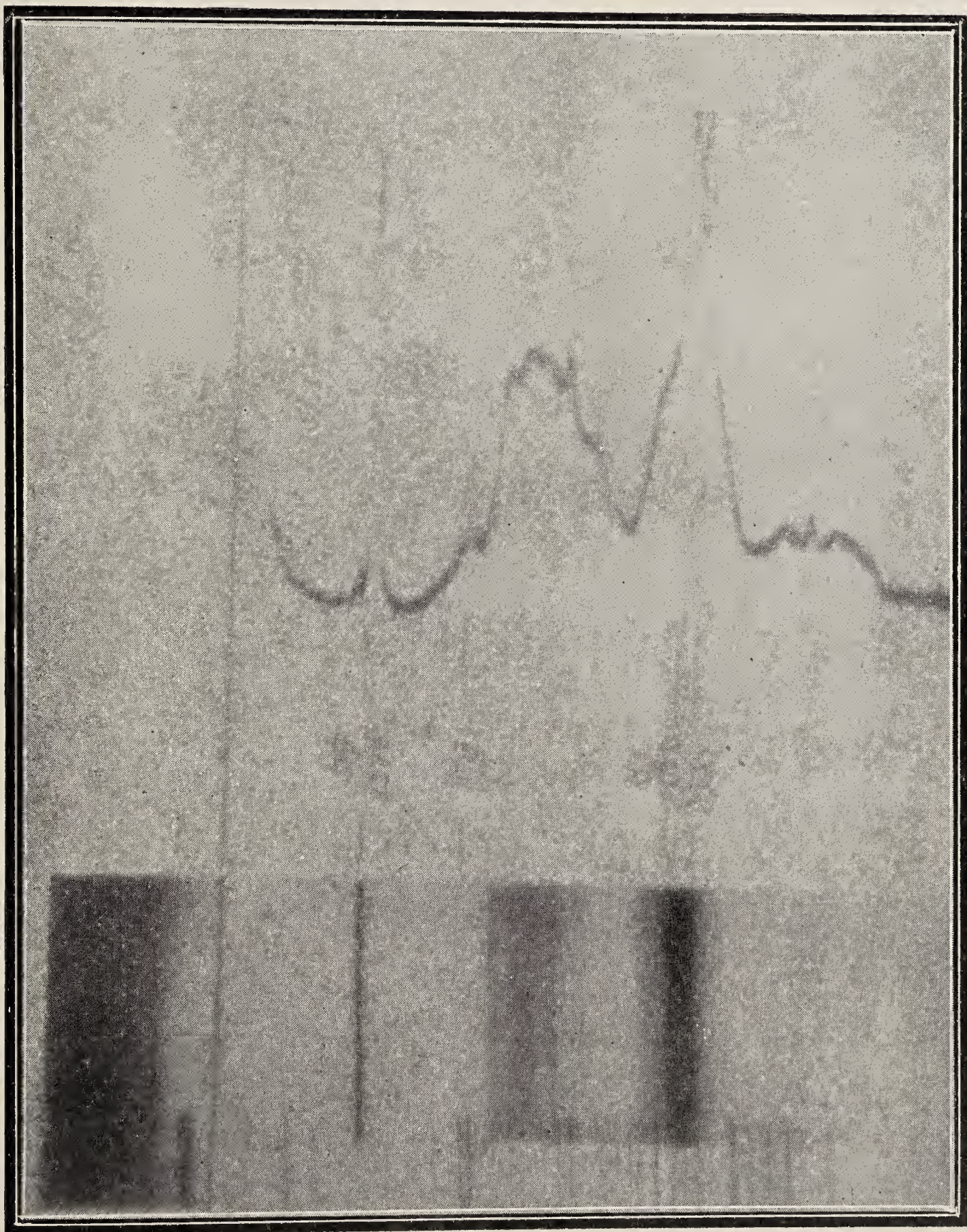


FIG. 1. Double-Frequency Shifts in Light-Scattering by Rock-Salt.







limiting value of 20% beyond  $100\ \mu$ . Infra-red activity arises from the movements of the electronic clouds in the crystal set up by the incident radiation. A complete independence of the normal modes of vibration and of their excitation cannot be assumed in these circumstances. That the different normal modes would co-operate to varying extents and that such excitation would manifest itself in the reflecting power of the crystal is only to be expected.

In determining the transmission by the thinnest films of NaCl, the fundamental absorption at  $55.6\ \mu$  would naturally play the leading role. But one cannot ignore the existence of other absorptions which would simultaneously operate. Amongst these are the modes which are active with doubled frequencies as stated above. We should also take account of the whole series of modes with greater wavelengths which may be simultaneously excited by the reason of the non-independence of normal modes. It would not be surprising if in these circumstances the wavelength of maximum absorption is shifted appreciably towards wavelengths greater than  $55.6\ \mu$ .



# THE SPECTROSCOPIC BEHAVIOUR OF ROCK-SALT AND THE EVALUATION OF ITS SPECIFIC HEAT

## Part IV. Specific Heat and Spectral Frequencies

BY SIR C. V. RAMAN

(*Memoir No. 128 of the Raman Research Institute, Bangalore-6*)

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### 1. INTRODUCTION

THE numerous published measurements of the thermal energy-content of crystalline solids and its variation with temperature make it clear that the theory of specific heats is concerned with the movements of the atomic nuclei in crystals about their positions of equilibrium and especially with the frequencies of their vibrations. A clear picture of the nature of these vibrations emerges if we take the basic facts of crystal architecture as our starting-point, viz., that a crystal consists of an immense number of similar and similarly situated units of structure. Each unit of structure contains a group of atomic nuclei which can interact with each other through the electrons which hold them together. The next step is to make use of the theory of small vibrations in classical mechanics to find the normal modes and frequencies of free vibration of these nuclei about their positions of equilibrium. In treating this problem, we have of necessity to recognise and take account of the three-dimensional periodicity of the crystal architecture. The principles of thermodynamics and of the quantum theory have then to be introduced and applied to the problem. They indicate that the normal modes deduced classically would be excited to various levels of energy, the relative probabilities of such excitation being determined by the respective energies and the absolute temperature. The average energy associated with each such normal mode and hence also the total average energy of all the normal modes taken together can then be computed. A multiplication of this average by the number of the oscillators in the crystal considered gives the total thermal energy of the solid as a function of the temperature.

It has been shown in the preceding parts of this memoir that a basically similar approach enables us to explain or elucidate the spectroscopic properties of the crystal. It follows that the thermal and spectroscopic behaviours



of the crystal stand in the closest relationship to each other. It should therefore be possible by making use of the spectroscopically determined frequencies of vibration to evaluate the specific heat of the crystal as a function of temperature and proceed to a comparison of the results thus obtained with the measured specific heats. No data are required for such an evaluation except those emerging from the spectroscopic studies. It follows that an agreement between theory and experiment would constitute a perfect demonstration of the correctness of the approaches made alike to spectroscopic theory and to the theory of specific heats.

## 2. THE SPECTRAL FREQUENCIES OF ROCK-SALT

In the case of magnesium oxide which has been dealt with in memoir No. 127 appearing in the same issue of these *Proceedings*, the spectroscopic frequencies were determined by the study of infra-red absorption in that crystal. In the case of rock-salt now considered, we have two distinct methods of investigation available which, as has already been noticed, give results supporting each other and confirming the inferences from theory. Of the two methods of study, *viz.*, infra-red spectroscopy and the scattering of light, the latter is definitely superior, since the data furnished by it are both complete and exact. All the nine modes appear in light-scattering with doubled frequency shifts with respect to the position in the spectrum of the  $\lambda$  2536.5 radiation of the mercury arc used to illuminate the crystal. The spectral shifts are recorded on both sides of the exciting radiation, and the microphotometer records of the spectrum on the two sides usefully supplement each other. On the heavily exposed side, the background due to the continuous radiation in the incident light is relatively less important, and the record therefore gives a truer picture of the spectrum taken as a whole. But, on the other hand, the heavy exposure results in obscuring finer detail and its microphotometer record fails to exhibit a complete resolution of the spectrum into its distinct components. The microphotometric record of the weakly exposed side is greatly superior in this respect. Not only does it reveal the nine distinct double-frequency shifts in the scattered light but also enables them to be read off directly from the record with tolerable accuracy.

Figure 1 in the text is the same record as that reproduced as Fig. 1 in the previous part of the memoir. But now the frequency shifts have been entered and shown against the visible peaks in the record which enabled them to be measured with reference to the position of the exciting radiation, the prominent  $235\text{ cm.}^{-1}$  shift being used to furnish the necessary scale of frequencies. The frequency shifts determined in this manner and entered



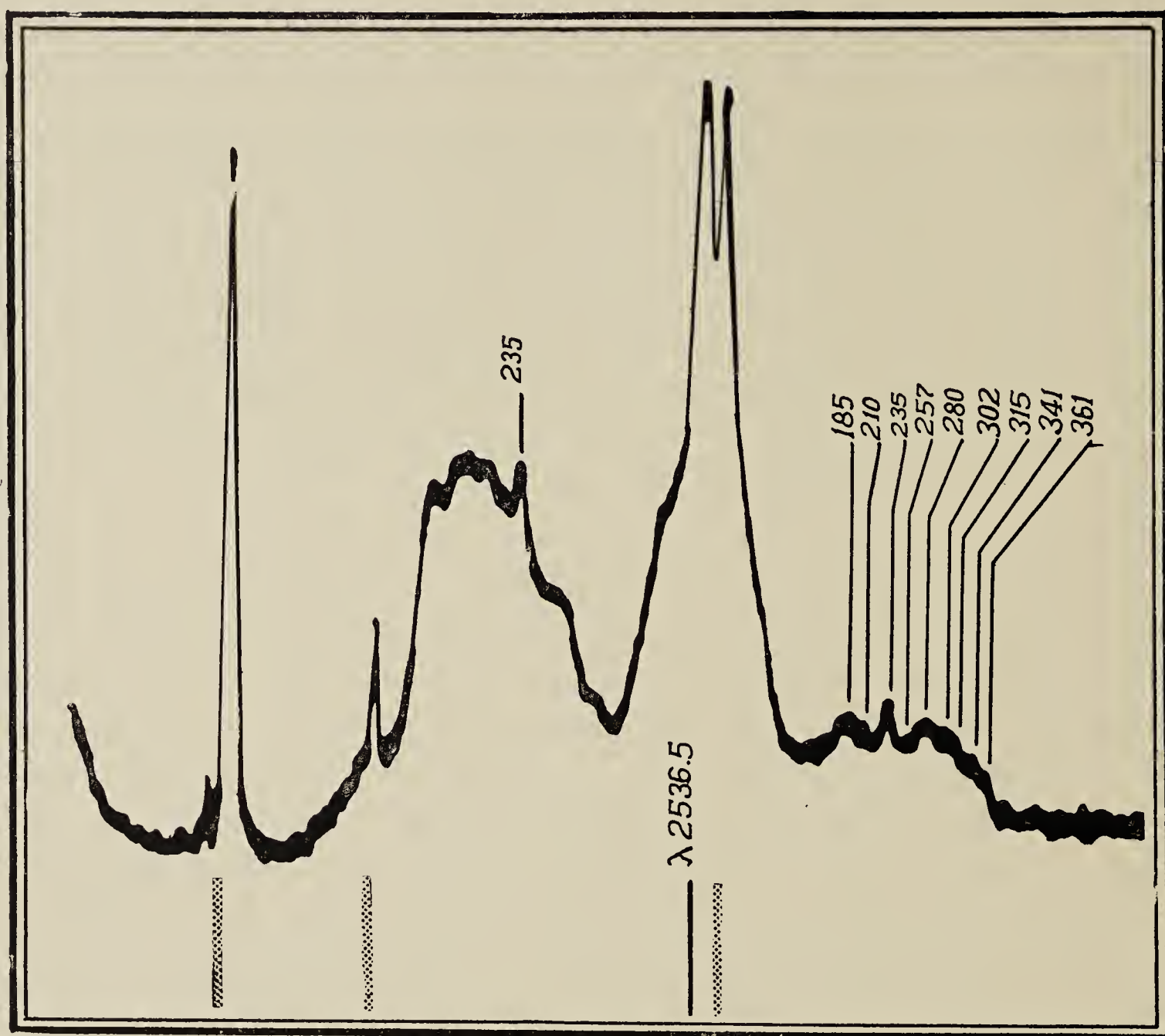


FIG. 1. Microphotometer Record showing frequency shifts.

in the figure differ little from those obtained by measurements under a micrometer of original spectrum plates recorded with rock-salt.

### 3. COMPARISON WITH THE SPECIFIC HEAT DATA

The manner in which we proceed from the spectroscopic frequencies to evaluate the specific heat of rock-salt as a function of the temperature is entirely analogous to that already fully explained for the case of MgO in a memoir appearing in the same issue of these *Proceedings*. It is unnecessary to traverse the ground here once again and it suffices to present a tabulation of the contributions to the specific heat made by the different normal modes of vibration, as also by the residual spectrum of vibration frequencies which is continuous and extends towards zero frequency. The normal frequencies of vibration made use of in the calculations are one-half the frequency shifts (in  $\text{cm}^{-1}$ ) observed in the scattering of light.

Though the structure of rock-salt is similar to that of MgO, the two cases differ in certain important respects. The vibration spectrum of rock-



salt lies much further out in the infra-red than that of  $\text{MgO}$ . As is to be expected in the circumstances, the increase in its specific heat from very low to normal values takes place for the most part in the region of liquid air and liquid hydrogen temperatures. Tabulations are therefore required in the case of rock-salt only for temperatures between 0 and 300 degrees absolute.

The foregoing remarks have some further implications. As has been pointed out in the third part of this memoir, the frequency shifts observed in light scattering exhibit a temperature effect. The frequency shifts broaden asymmetrically and also move to smaller values as the temperature is raised. In the case of rock-salt, the spectroscopic data we make use of were obtained with the crystal held at room temperature. Hence, it cannot be expected that these data would fit the specific heat curve at very low temperatures and especially at the temperatures where the specific heat changes most rapidly. We could only expect the theoretically calculated specific heats for low temperatures to agree with observed specific heats if the frequencies used had been determined with the crystal held at the same temperatures.

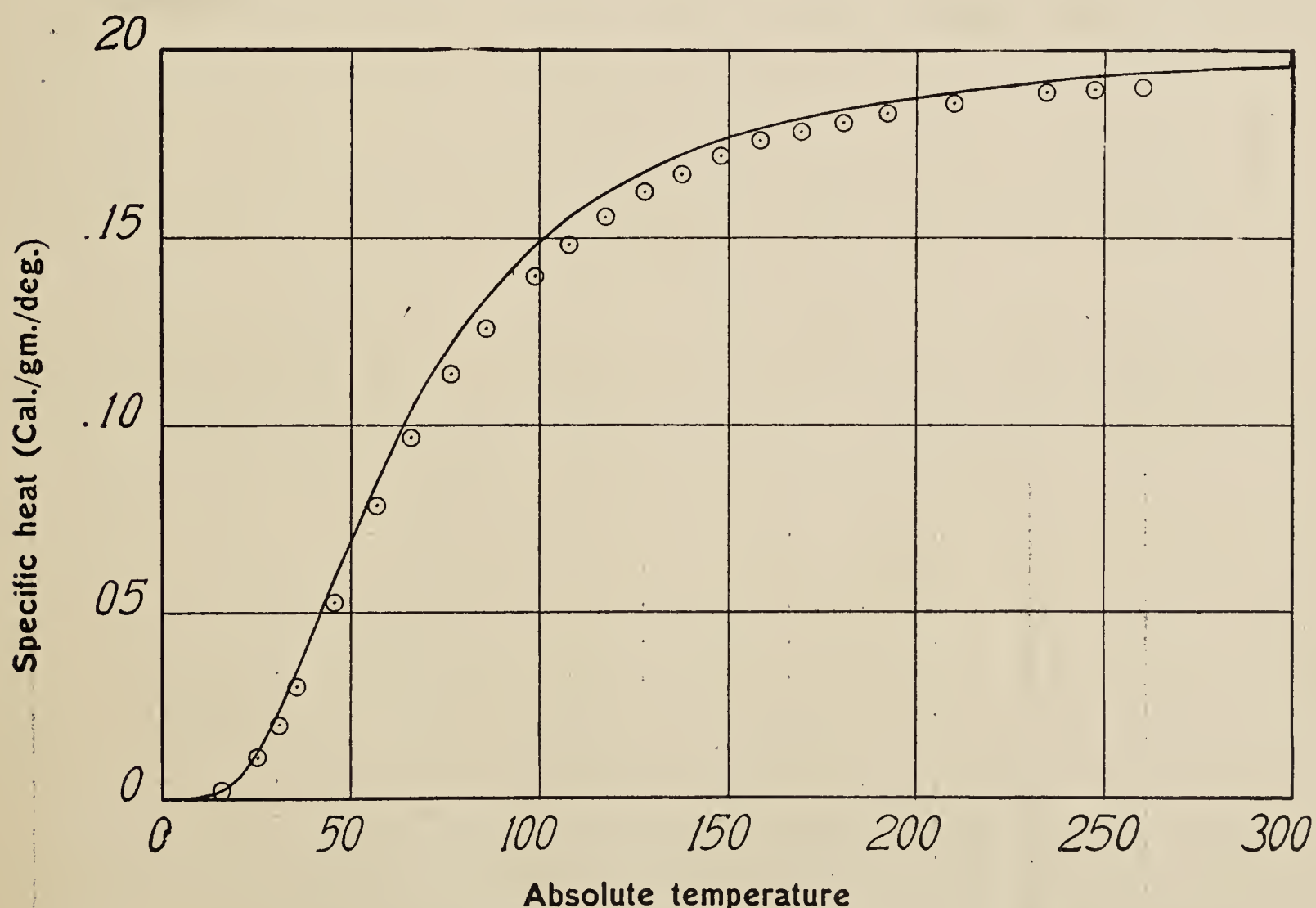


FIG. 2. Comparison of theory and experiment. Theory —. Experiment  $\odot \odot \odot$ .

The foregoing remarks find support in the results of the actual computations. Tables I and II show the specific heats as computed and the



TABLE I

*Computation of the specific heats*

	10° K	15° K	25° K	50° K	75° K	100° K	125° K
$3E_1$ (180 cm. <sup>-1</sup> )	..	..	0.0023	0.1088	0.2929	0.4312	0.5223
$4E_2$ (170 cm. <sup>-1</sup> )	..	..	0.0047	0.1738	0.4278	0.6091	0.7235
$8E_3$ (157 cm. <sup>-1</sup> )	..	0.0001	0.0176	0.4359	0.9638	1.3059	1.5135
$6E_4$ (150 cm. <sup>-1</sup> )	..	0.0001	0.0181	0.3673	0.7652	1.0137	1.1610
$4E_5$ (140 cm. <sup>-1</sup> )	..	0.0002	0.0188	0.2876	0.5545	0.7099	0.7994
$3E_6$ (129 cm. <sup>-1</sup> )	..	0.0004	0.0226	0.2571	0.4517	0.5593	0.6180
$8E_7$ (118 cm. <sup>-1</sup> )	..	0.0026	0.0960	0.8042	1.3013	1.5608	1.6985
$3E_8$ (110 cm. <sup>-1</sup> )	..	0.0019	0.0502	0.3362	0.5154	0.6043	0.6506
$6E_9$ (92 cm. <sup>-1</sup> )	0.0004	0.0156	0.2056	0.8453	1.1482	1.2852	1.3569
$3D$ (92 cm. <sup>-1</sup> )	0.0240	0.0767	0.2458	0.5332	0.6378	0.6818	0.7036
Molecular heat (cal./gm./deg.)	0.0244	0.0976	0.6817	4.1494	7.0586	8.7612	9.7473
Specific heat (cal./gm./deg.)	0.0004	0.0017	0.0117	0.0710	0.1208	0.1499	0.1668



TABLE II

*Computation of the specific heats*

	150° K	175° K	200° K	225° K	250° K	275° K	300° K
$3E_1$ (180 cm. <sup>-1</sup> ) .. ..	0.5805	0.6195	0.6468	0.6647	0.6805	0.6909	0.6983
$4E_2$ (170 cm. <sup>-1</sup> ) .. ..	0.7952	0.8416	0.8738	0.9005	0.9156	0.9283	0.9377
$8E_3$ (157 cm. <sup>-1</sup> ) .. ..	1.6398	1.7249	1.7807	1.8229	1.8510	1.8753	1.8927
$6E_4$ (150 cm. <sup>-1</sup> ) .. ..	1.2507	1.3084	1.3528	1.3776	1.3965	1.4125	1.4248
$4E_5$ (140 cm. <sup>-1</sup> ) .. ..	0.8530	0.8863	0.9114	0.9269	0.9390	0.9487	0.9554
$3E_6$ (129 cm. <sup>-1</sup> ) .. ..	0.6542	0.6774	0.6920	0.7023	0.7106	0.7166	0.7204
$8E_7$ (118 cm. <sup>-1</sup> ) .. ..	1.7807	1.8340	1.8673	1.8903	1.9087	1.9211	1.9326
$3E_8$ (110 cm. <sup>-1</sup> ) .. ..	0.6785	0.6941	0.7063	0.7141	0.7197	0.7241	0.7274
$6E_9$ (92 cm. <sup>-1</sup> ) .. ..	1.3945	1.4178	1.4347	1.4455	1.4535	1.4599	1.4644
$3D$ (92 cm. <sup>-1</sup> ) .. ..	0.7159	0.7229	0.7281	0.7314	0.7338	0.7357	0.7370
Molecular heat .. ..	10.3430	10.7269	10.9939	11.1762	11.3089	11.4131	11.4907
Specific heat (cal./gm./deg.) .. ..	0.1770	0.1835	0.1881	0.1912	0.1935	0.1953	0.1966



TABLE III  
*Computation of the specific heats*

	10° K	15° K	25° K	50° K	75° K	100° K	125° K
$3E_1$ (189 cm. <sup>-1</sup> ) .. ..	..	..	0·0015	0·0925	0·2678	0·4058	0·5034
$4E_2$ (179 cm. <sup>-1</sup> ) .. ..	..	..	0·0031	0·1478	0·3944	0·5794	0·6986
$8E_3$ (165 cm. <sup>-1</sup> ) .. ..	..	0·0001	0·0121	0·3804	0·8966	1·2504	1·4693
$6E_4$ (158 cm. <sup>-1</sup> ) .. ..	..	0·0001	0·0125	0·3212	0·7165	0·9725	1·1318
$4E_5$ (147 cm. <sup>-1</sup> ) .. ..	..	0·0001	0·0138	0·2576	0·5233	0·6872	0·7804
$3E_6$ (135 cm. <sup>-1</sup> ) .. ..	..	0·0002	0·0175	0·2339	0·4312	0·5443	0·6073
$8E_7$ (124 cm. <sup>-1</sup> ) .. ..	..	0·0017	0·0749	0·7360	1·2504	1·5223	1·6715
$3E_8$ (116 cm. <sup>-1</sup> ) .. ..	..	0·0012	0·0392	0·3104	0·4949	0·5901	0·6412
$6E_9$ (97 cm. <sup>-1</sup> ) .. ..	0·0002	0·0106	0·1674	0·7949	1·1153	1·2624	1·3416
$3D$ (97 cm. <sup>-1</sup> ) .. ..	0·0204	0·0665	0·2213	0·5146	0·6270	0·6746	0·6991
Molecular heat .. ..	0·0206	0·0805	0·5633	3·7893	6·7174	8·4890	9·5442
Specific heat (cal./gm./deg.) .. ..	0·0004	0·0014	0·0096	0·0648	0·1149	0·1452	0·1633



TABLE IV  
Computation of the specific heats

	150° K	175° K	200° K	225° K	250° K	275° K	300° K
$3E_1$ (189 cm. <sup>-1</sup> ) .. ..	0.5659	0.6073	0.6370	0.6566	0.6754	0.6856	0.6941
$4E_2$ (179 cm. <sup>-1</sup> ) .. ..	0.7761	0.8280	0.8625	0.8883	0.9087	0.9213	0.9323
$8E_3$ (165 cm. <sup>-1</sup> ) .. ..	1.6113	1.6985	1.7603	1.8092	1.8397	1.8620	1.8833
$6E_4$ (158 cm. <sup>-1</sup> ) .. ..	1.2268	1.2909	1.3355	1.3672	1.3883	1.4045	1.4178
$4E_5$ (147 cm. <sup>-1</sup> ) .. ..	0.8397	0.8754	0.9046	0.9213	0.9337	0.9440	0.9522
$3E_6$ (135 cm. <sup>-1</sup> ) .. ..	0.6468	0.6708	0.6878	0.6983	0.7071	0.7133	0.7181
$8E_7$ (124 cm. <sup>-1</sup> ) .. ..	1.7572	1.8201	1.8567	1.8833	1.9020	1.9149	1.9273
$3E_8$ (116 cm. <sup>-1</sup> ) .. ..	0.6708	0.6888	0.7013	0.7106	0.7166	0.7212	0.7254
$6E_9$ (97 cm. <sup>-1</sup> ) .. ..	1.3840	1.4105	1.4283	1.4409	1.4495	1.4574	1.4621
$3D$ (97 cm. <sup>-1</sup> ) .. ..	0.7126	0.7207	0.7261	0.7300	0.7326	0.7350	0.7364
Molecular heat .. ..	10.1912	10.6110	10.9001	11.1057	11.2536	11.3592	11.4490
Specific heat (cal./gm./deg.) .. ..	0.1744	0.1815	0.1865	0.1900	0.1925	0.1943	0.1959



TABLE V  
*Experimental data of specific heats*

Temperature	10.9° K	15.3° K	25.1° K	50.7° K	76.4° K	103.1° K
Molecular heat ..	0.044	0.134	0.658	3.820	6.626	8.424
Specific heat .. (cal./gm./deg.)	0.0008	0.0023	0.0113	0.0654	0.1134	0.1441

Temperature	127.7° K	153.2° K	174.9° K	198.1° K	222.5° K	253.9° K	260.6° K
Molecular heat ..	9.486	10.162	10.542	10.792	11.006	11.104	11.134
Specific heat .. (cal./gm./deg.)	0.1623	0.1739	0.1804	0.1846	0.1883	0.1900	0.1905

(Experimental values of specific heat of NaCl taken from K. Clusius, J. Goldmann and A. Perlick, *Z. Naturforschg*, 1949, 4 A, 424-432.)



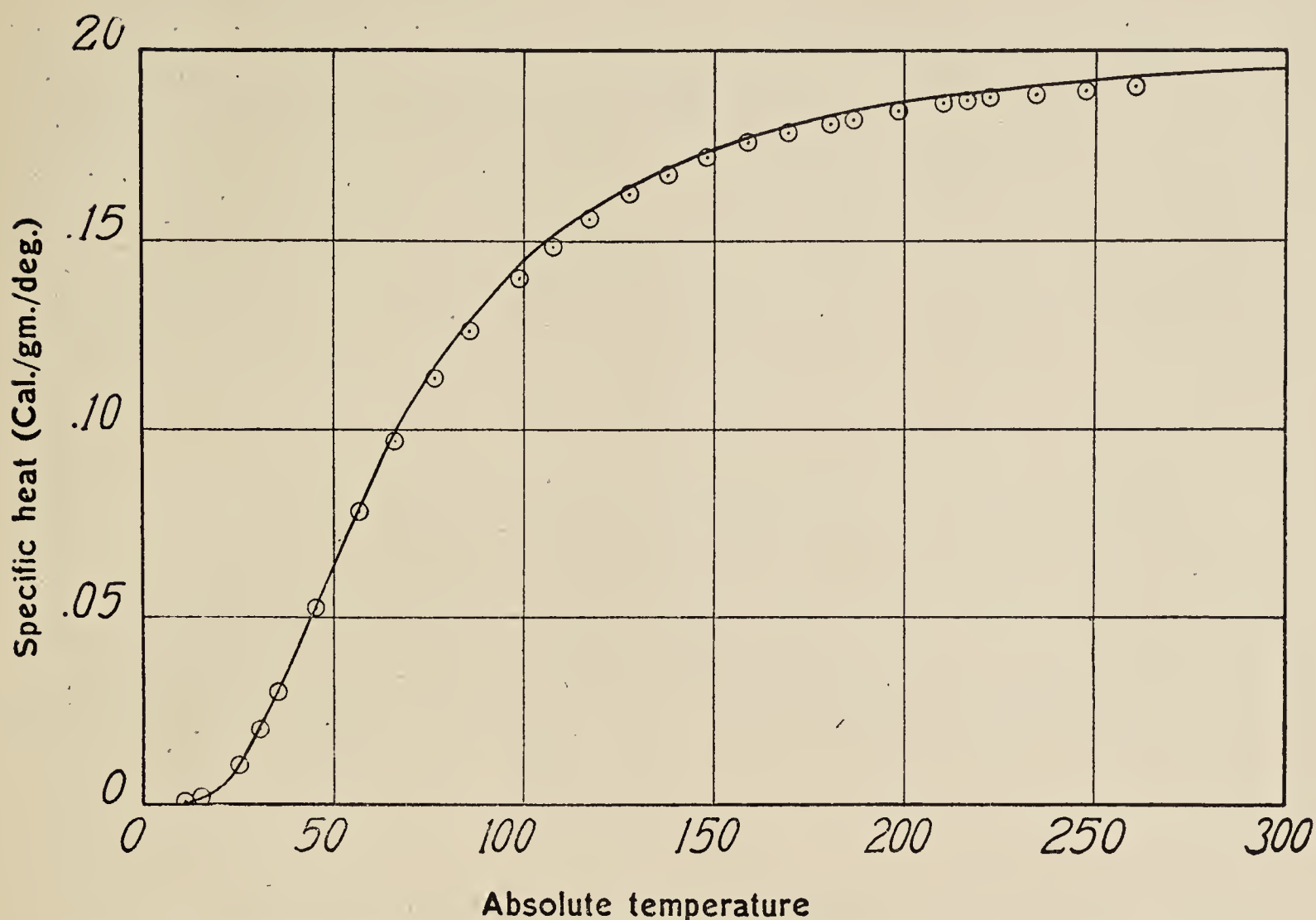


FIG. 3. Comparison of theory and experiment. Theory —. Experiment  $\odot \odot \odot$ .

results have been drawn as a continuous graph in Fig. 2 in the text. The experimental values in the same range of temperatures are given in Table V and have been shown as dotted circles in Fig. 2. It will be seen that the experimental values lie systematically below the theoretical curve, the deviations being greatest in the range between 50 and 150 degrees absolute.

The differences between theory and experiment indicated in Fig. 2 arise, without doubt, by reason of the spectroscopic frequencies used in the calculations being less than the actual spectroscopic frequencies at low temperatures. Precisely what the latter are cannot be stated on the basis of present knowledge. Any attempt to fit theory and experiment by using assumed values for the frequencies might well be thought artificial and unsatisfactory. It appeared however useful to present a second set of computations in which all the frequencies made use of are raised uniformly by 5% of their respective values. Such an increase is certainly not greater than would be justified by a comparison with those cases, *e.g.*, quartz and calcite, where the effect of using liquid air temperatures on the vibration frequencies has been quantitatively studied. The fresh computations on this basis have been shown in Tables III and IV, and their results plotted in Fig. 3 against the experimental results. The greatly improved agreement between theory and experiment which is exhibited in Fig. 3 makes it clear



that the lack of such agreement appearing in Fig. 2 is due to the frequencies made use of in that case not being the actual frequencies. Indeed, a perfect fit with the experimental data could have been obtained by appropriate alterations in the frequencies made use of in the calculations. But it did not appear worthwhile to attempt to do this for the reason that Figs. 2 and 3 by themselves make it perfectly clear that the approach to the specific heat theory made in the present investigation is essentially a complete success.

#### 4. SUMMARY

The spectroscopically determined vibration frequencies of the rock-salt structure are made use of for a theoretical evaluation of its specific heat as a function of temperature. The results thus obtained are compared with the measured specific heats. The agreement between theory and experiment which emerges demonstrates the correctness of the approaches made alike to spectroscopic theory and to the theory of specific heats.



# THE SPECIFIC HEATS OF CRYSTALLINE SOLIDS: PART I\*

BY SIR C. V. RAMAN

(Memoir No. 101 of the Raman Research Institute, Bangalore-6)

A CORRECT appreciation of the nature of the thermal agitation in a crystal is obviously of fundamental importance in the physics of the solid state. Closely related to it is the problem of evaluating the heat content of a crystalline solid as a function of the temperature. These topics have formed the subject of some recent studies by the present writer. From them has emerged a theory of the specific heats of crystalline solids which is both simple and comprehensive and which succeeds in establishing a quantitative relationship between the thermal properties and the spectroscopic behaviour of crystals and accounts for the facts of observation in both of these fields. It accordingly seems opportune to offer a connected review of the subject in which the basic principles are set forth as simply and clearly as possible.

## 2. SOME GENERAL CONSIDERATIONS

A crystal is an assembly of great numbers of atoms (of the same or of several different species) in a three-dimensionally periodic array in space. Macroscopically regarded, a crystal of finite size is a single physical entity; and those problems concerning its physical behaviour in which the discrete atomic structure does not need to be specifically considered can be dealt with on that basis. But neither the evaluation of the thermal energy of the solid nor the determination of its spectroscopic behaviour is a problem of that nature. For, the discrete atomic structure of the solid is the very essence of both of these problems and it must therefore form the basis of any theoretical considerations regarding them. It is therefore a misconceived and irrational procedure to assume—as is done in the theories of Debye and Born—the macroscopic crystal to be itself the oscillating unit whose modes and frequencies of vibration determine the thermal properties and the spectroscopic behaviour of the solid. While we have necessarily to reject such an approach as inadmissible, we are also precluded from assuming that the individual atoms in the crystal are the oscillators with which we are concerned. This is obvious, for the atoms in a crystal are linked together by forces of a physico-chemical nature and hence they cannot oscillate independently of each other.

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\* Reprinted from *Current Science* for July 1957.



Thus, when both of these extreme suppositions are laid aside, we are left with the following questions requiring an answer. What are the oscillators which determine the thermal properties and the spectroscopic behaviour of a crystal? How are they to be enumerated, and in what manner are their modes and frequencies of vibration to be determined? The answers given to these questions stand at the very base of the problems now under consideration.

### 3. THE NORMAL MODES OF VIBRATION

The fundamental theorem in classical mechanics regarding the small vibrations of a system of connected particles, taken in conjunction with the three-dimensional periodicity of structure characteristic of the crystalline state, furnishes us with the key to the solution of our problem. The theorem referred to states that the possible vibrations of the system are superpositions of a set of normal modes, in each of which the particles of the system (in the present case, the atoms) vibrate with the same frequency and in the same or opposite phases. Hence, any mode of vibration which satisfies this description and which can be regarded as a characteristic property of the crystal must also satisfy the further criterion that it remains the same when the crystal is given a unit translation along any one of the three axes of its structure. This can obviously happen in two ways: following the unit translation, equivalent atoms in the adjacent cell retain their amplitudes and phases of vibration unaltered, or alternatively, while the amplitudes remain the same, the phases are all reversed. Thus, we have  $2 \times 2 \times 2$  or 8 different possible situations. If there are  $p$  atoms in each unit cell of the crystal structure, each of the 8 possible situations give us  $3p$  solutions of the equations of motion of the  $p$  atoms in the unit cell, in other words, indicates  $3p$  normal modes of vibration with their respective frequencies which can be regarded as characteristic of the structure of the crystal. Thus, in all, we have  $24p$  solutions of the equations of motion which may be divided into three groups: ( $3p - 3$ ) normal modes in which equivalent atoms in adjacent cells oscillate with identical amplitudes and phases;  $21p$  other normal modes in which the amplitudes of equivalent atoms in adjacent cells are the same but their phases alternate along one, two or all three of the axes of the crystal structure; and finally, the 3 excluded translations.

### 4. THE OSCILLATORS AND THEIR ENUMERATION

We proceed to consider the physical significance of the results deduced and stated above. What they indicate is that we shall not be justified in identifying the groups of  $p$  atoms each which form the units of the crystal structure as the "oscillators" in specific heat theory, since their juxtaposition in the ordered structure of the crystal results in an eight-fold increase in



the number of distinct frequencies of internal vibration which these groups of  $p$  atoms each would possess if isolated from each other. We have also to recognize the existence of additional modes of vibration within the crystal made possible by the translatory movements of the atomic groups as distinct from their internal vibrations. It is to be remarked, however, that the  $(24p - 3)$  normal modes of vibration with discrete frequencies indicated by the theory can be regarded as the *internal* modes of vibration of the groups of  $8p$  atoms each to be found in volume elements whose dimensions are twice as large in each direction as those of the unit cells of the crystal structure. If the entire crystal encloses  $N$  unit cells, the number of groups of  $8p$  atoms included in it would be  $N/8$ . Multiplying this by  $(24p - 3)$  which is the number of their internal modes of vibration, and adding to the product the number of degrees of the translatory freedom of movement of the same groups, we recover  $3Np$ , which is the total of the number of degrees of freedom of atomic movement in the crystal.

## 5. THE VIBRATION SPECTRA OF CRYSTALS

Thus, the atomistic approach to specific heat theory leads us directly to a result which is of fundamental importance in relation to the spectroscopic behaviour of crystals, namely, that by far the largest proportion of the atomic degrees of freedom of movement in crystals is manifested in their vibration spectra as a set of discrete monochromatic frequencies  $(24p - 3)$  in number,  $p$  being the number of atoms in the unit cell, only the three omitted translations manifesting themselves in what may be designated as the “residual spectrum” comprising the lowest frequencies of vibration and having a different character which we shall consider presently. The nature of the vibration spectrum of a crystal as stated above which is indicated by the theory might have been anticipated *a priori* on general grounds. For, a crystal comprises within itself an immense number of similar and similarly situated groups of atoms which would necessarily be of identical dynamical behaviour. Hence, the modes and frequencies of internal vibration of these groups would all be the same and would be a characteristic property of the crystal. The reason why we have  $(24p - 3)$  discrete frequencies and not  $(3p - 3)$  is also readily understood. The additional  $21p$  frequencies arise because of the coupling of the oscillators located along each of the axes of the structure, an effect analogous to that observed in the simple case of two similar oscillators which when coupled to each other exhibit two distinct frequencies of vibration instead of only one.

We must now consider the nature of the “residual spectrum” briefly alluded to above. This spectrum embodies the oscillatory movements arising



from the *translations* of volume elements of the crystal each containing  $8p$  atoms; they may be described as *internal vibrations* in volume elements of still larger size and therefore having lower frequencies. The frequency  $\nu$  of such a vibration can evidently range from a lower limit  $\nu = 0$  to the upper limit  $\nu = \nu_L$ ,  $\nu_L$  being the lowest of the  $(24p - 3)$  discrete frequencies of atomic vibration. The manner in which the disposable  $3N/8$  degrees of freedom would be distributed over this range of frequencies can be deduced by a very simple argument. The total number of volume elements of any specified dimensions included in the crystal, and therefore also the number of degrees of freedom represented by their *translations* would diminish in inverse proportion to the cube of their linear dimensions, while the frequencies of their *internal vibrations* would vary inversely as the first power of the same. Hence the number of degrees of freedom appearing in the residual spectrum in the range of frequencies between 0 and  $\nu$  would be proportional to  $\nu^3$ . By differentiation, we obtain the result that the number of degrees of freedom appearing between frequencies  $\nu$  and  $\nu + d\nu$ , in other words, the number of oscillators in the crystal having frequencies in that range, would be  $3N/8 \times 3\nu^2 d\nu / \nu_L^3$ .

## 6. QUANTISATION OF THE VIBRATIONAL ENERGY

In his classic paper of 1907 introducing the quantum theory of specific heats, Einstein showed that the acceptance of his theory of light quanta inevitably leads to the conclusion that the energy of the mechanical vibration of elementary oscillators—such as the molecules of a gas or the structural units in a crystal—would also be related to their respective frequencies by the quantum rules. He also indicated a procedure by which the thermal energy of a crystal could be evaluated as a function of the temperature on the basis of the quantum hypothesis. He identified the thermal energy of the crystal with the energy of mechanical vibration of an immense number of *individual* oscillators distributed over its volume. It was assumed that these oscillators could be grouped into sets, each set comprising a great number of individual oscillators characterised by a common frequency of vibration. The total number of the oscillators of all kinds was taken to be equal to thrice the number of the atoms comprised in the crystal. The oscillators themselves were assumed to be harmonic and to occupy the various energy levels allowed by the quantum hypothesis for the particular frequency. The thermodynamic principle of Boltzmann was then introduced, leading to the result that the numbers of the oscillators occupying the various permitted levels are in the relative proportions indicated by that principle, and determined by the respective energies and by the temperature. The average energy of the oscilla-



tors in each of the sets was then evaluated. Summing up over all the oscillators in each of the sets and then over all the sets, Einstein obtained an explicit formula for the thermal energy of a crystal as a function of the temperature.

Einstein's ideas necessarily form the basis of any rational approach to the solution of the specific heat problem for crystals. For, they are based on an atomistic approach to the problem and effect a synthesis of the results of classical dynamics with the notions of the quantum theory and the basic principles of thermodynamics, in other words, of all the three disciplines which find a place in the problem. Einstein's formulation, however, had the weakness that he left unanswered three important questions: What precisely are the individual oscillators contemplated in the theory? How are they to be enumerated? How should their frequencies of vibration be determined? Also, to enable his theory to be applied in the particular case of diamond, Einstein assumed that the individual atoms in that crystal were themselves the oscillators contemplated in his theory. This was an oversimplification which resulted in discrediting Einstein's theory. For, that assumption was theoretically unsustainable and it also led to values for the specific heats at low temperatures which were in disagreement with the experimental facts elicited by later investigations. It is not surprising in these circumstances that Einstein's approach to the specific heat problem was laid aside, and that other and totally different ways of approaching the same problem gained general acceptance.

The present approach to specific heat theory is in a sense a rehabilitation of Einstein's original ideas. It fills in the lacunæ left by him and we are thereby enabled to make use of Einstein's formulæ just as they stand for an evaluation of the thermal energy of the crystal. But, before we proceed to write down the expressions, it appears desirable to emphasize certain fundamental aspects of Einstein's theory which also find a place in the present approach to the subject. Einstein's application of Boltzmann's statistical-thermodynamical principle finds its logical justification in the fact that the crystal is regarded as an assembly of great numbers of similar oscillators capable of exchanging energy with each other and forming a system in thermodynamic equilibrium. The use of the principle implies that the energy of vibration of the individual oscillators of each sort exhibits fluctuations over the volume of the crystal both in space and in time, the magnitude of these fluctuations being naturally the greater, the higher the frequency of the oscillator considered. This picture of the thermal agitation in crystals is fundamentally in accord with the actual facts of crystal architecture as well as with



the principles of thermodynamics, but it is very remote indeed from any ideas of its nature based on the notions of macroscopic physics.

Another feature of Einstein's theory which he himself stressed is the intimate relationship which it indicates between the thermal properties and the spectroscopic behaviour of crystals. The same relationship is also a feature of the present theory. But, the latter goes further than Einstein's, since it specifies the number of sets of oscillators which are the carriers of the thermal energy and also indicates the procedure by which their frequencies may be evaluated. Properties descriptive of the macroscopic behaviour of solids, *viz.*, their elastic constants, do not as such find a place in the present theory of the specific heats of crystals.

## 7. EVALUATION OF THE SPECIFIC HEATS OF CRYSTALS

Making use of the reasoning employed by Einstein, we obtain the following expression for the heat content of a volume of a crystal containing  $N$  unit cells of the crystal structure as a function of the temperature, namely

$$\frac{N}{8} \left[ \sum_{i=1}^{24p-3} \frac{h\nu_i}{e^{h\nu_i/KT} - 1} + \frac{3}{\nu_L^3} \cdot \int_0^{\nu_L} \frac{3h\nu^3 d\nu}{e^{h\nu/KT} - 1} \right]$$

The numerical factor  $1/8$  appears in the expression because each oscillator comprises 8 unit cells of the crystal structure. On differentiating the expression with respect to  $T$ , we obtain the formula for the specific heat.

The following remarks may be made regarding the numerical evaluation of the expression given above. All the  $(24p - 3)$  frequencies would be distinct from each other only in the case of a completely anisotropic crystal. If any symmetry elements are present, the number of distinct frequencies would be naturally diminished, but the formula remains the same. Such reduction in the number of distinct frequencies would appear both in respect of the  $(3p - 3)$  frequencies in which both the amplitudes and the phases are the same in adjacent unit cells and in the  $21p$  others in which the phases may be opposite, as already explained. As an illustration of these remarks, we may consider a case in which  $p = 2$  and the crystal belongs to the cubic class and its structure consists of two interpenetrating face-centred cubic lattices. The  $(3p - 3)$  distinct frequencies then reduce to a single triply degenerate frequency: the  $21p$  or 42 other vibrations reduce to only eight distinct frequencies, the modes relating to all of which may be readily described in geometric terms connected with the structure of the crystal.



Since the first term in the expression for the thermal energy is a summation extended over  $(24p - 3)$  distinct modes of vibration, while the second represents the residual spectrum, it is evident that the latter would be of minor importance relatively to the first, especially in those cases where  $p$  is large, in other words when the crystal has a multi-atomic structure. The position is a little different when  $p$  is small, as for example, when  $p$  is equal to 1. The contribution from the second term would not then be altogether negligible in comparison with the first term. The second term also acquires some importance relatively to the first at very low temperatures. For, since the frequencies appearing in it are low, their contributions to the specific heat would survive when those due to the vibrations of the higher frequencies appearing in the first term have dropped out by reason of Boltzmann's principle.



# THE SPECIFIC HEATS OF CRYSTALLINE SOLIDS: PART II\*

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THE theory of the specific heats of crystals expounded in the first part of this review is similar in its approach to that originally proposed by Einstein in the year 1907, but it fills up the lacunæ left in that theory and succeeds in connecting the thermal energy of crystals with their spectroscopic behaviour, as also in explaining the facts of observation in both of these fields. It is hoped on some later occasion to set out the results following from the theory in greater detail and to illustrate them by specific examples. The present review will conclude with some comments on the theory of the specific heats of crystals put forward by Debye in the year 1912 and the closely analogous theory published by Born and Karman at about the same time. A whole generation of physicists and chemists has been persuaded to believe that these theories embody valid physico-mathematical thought and that they satisfactorily account for the facts of observation. These are circumstances which justify the inclusion in the present review of some critical remarks on those theories.

## 2. THE FUNDAMENTALS OF SPECIFIC HEAT THEORY

We may usefully commence our examination by recalling the ideas embodied in Einstein's paper of 1907 in the form of three distinct<sup>t</sup> propositions.

I. A crystal is an assembly in thermodynamic equilibrium of an immense number of individual oscillators which are divisible into sets, each set consisting of a great number of oscillators characterised by a common frequency of vibration.

II. The total number of oscillators of all sorts is equal to thrice the number of atoms comprised in the crystal.

III. The vibrational energy of each individual oscillator is quantised and its average value taken over its different possible energy states may be determined by the aid of Boltzmann's principle.

The first of these propositions finds its justification in the known physical features of crystal architecture. The second proposition follows as a logical deduction from the first taken in conjunction with the results of classical

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mechanics. The third proposition is a logical consequence of the principles of thermodynamics and the quantum theory when applied to the circumstances stated in the first proposition. In the earlier part of this review, it has already been shown how these propositions enable us to deduce both the thermal and the spectroscopic behaviour of crystals.

### 3. THE THEORIES OF DEBYE AND BORN

The basic idea underlying these other theories is that the thermal energy of a crystal may be evaluated in the same manner as the energy density of thermal radiation within a perfectly reflecting enclosure, in other words, by summing up the kinetic and potential energies of sets of wave-trains which are assumed to fill the volume of the solid and form stationary wave-patterns in its interior. J. H. Jeans who was the original proposer of this idea indicated in his paper of 1909 a way of escape from the more obvious difficulties which arise when it is sought to make use of it. Debye and Born who derived their inspiration from Jeans naturally also took over from his paper the special assumptions needed to put his ideas into quantitative form. These special assumptions figure prominently in both of the theories and are indeed their most characteristic feature.

The stationary wave-patterns considered by Debye were those contemplated in the classical theory of elasticity for a solid of finite volume. An enumeration on the basis of that theory shows the total number of modes of vibration to increase—without any upper limit—proportionately to the cube of the frequency up to which the enumeration is carried. To enable the enumeration thus made to form the basis of specific heat theory, Debye assumed that the enumeration is valid only up to a certain upper limit of frequency and that no modes of vibration with higher frequencies exist; the upper limiting frequency was so chosen that the number of wave-patterns is equal in number to thrice the number of atoms comprised in the crystal.

The waves considered by Born are of a more general type than those considered in the Debye theory. Whereas Debye limited himself to the consideration of crystals of comparatively simple type, *viz.*, those containing a single species of atom and belonging to the cubic system, the theory of Born accepts no such limitation and indeed claims to be applicable to all crystals. The special assumption which figures in the Born theory is the well-known “cyclic postulate” which selects the permitted wave-lengths of the stationary wave-patterns filling the solid in such manner that the total number of wave-patterns is equal to thrice the number of atoms comprised in the crystal.



The questions which arise and which need to be considered are the following: Are the approaches to specific heat theory briefly summarized above logically sustainable? Are the ideas on which they are based and the conclusions to which they lead compatible with the fundamental principles of classical mechanics, thermodynamics and the quantum theory? We shall consider these questions and presently find that the answer is in each case definitely in the negative.

#### 4. THE LOGICAL FALLACY

A simple calculation shows that the frequencies of vibration which determine the variation of the specific heats of crystals with temperature lie in the infra-red region of the spectrum. It follows that the oscillators which are the carriers of the thermal energy are the ultimate structural elements in the crystal. This is further confirmed by the fact that when the atoms are firmly bound together in the structural elements of the crystal, as is the case for example with diamond, the specific heats are low and the vibrational frequencies estimated from them are high; the latter inference receives direct support from spectroscopic studies. It follows from these remarks that the approach to the specific heat problem made in the theories of Debye and Born is totally misconceived. These authors concern themselves with an entirely different and irrelevant subject, namely, the vibrations of a macroscopic solid and proceed to determine and enumerate them, treating it as a boundary-value problem in wave-propagation. It is easily shown that the results thus obtained are wholly unrelated to the specific heat problem. We have only to recall that wave-motion is a kinematic concept. Hence the stationary wave-patterns inside an enclosure can be described in purely geometric terms without any reference to the question whether the material traversed by the waves does or does not possess a discrete structure. In other words, there is no nexus or connection between the stationary wave-patterns assumed to exist in the medium and the discrete structure, if any, which it possesses. It is not surprising in these circumstances that Debye and Born are obliged to introduce postulates into their theories which assume the existence of such a relationship. We have only to remark that such postulates or assumptions savour of sophistry and that theories embodying them can lay no claim to logical validity.

#### 5. FALSITY OF THE DYNAMICAL CONSEQUENCES

The theories of Debye and Born are attempts to carry over the ideas and methods of macroscopic physics into the fields of atomic dynamics, thermodynamics and quantum theory where they are inappropriate and indeed wholly out of place. The procedures they adopt naturally lead to consequences



which are irreconcilable with the basic principles of these disciplines and the results following from them.

Considering the matter first from the standpoint of atomic dynamics, it is clear that we are not concerned here either with wave-propagation or with any boundary value problem. Specific heat theory rests on the determination and enumeration of the normal modes of vibration of the ultimate particles of the material, in other words, of the atoms present in the structure of the crystal. Since the range of the interatomic forces is limited and small compared with the dimensions of any crystal of macroscopic size, these normal modes are determinable from the structure of the crystal without any reference to the size of the crystal or to the conditions at its external boundary. This also becomes evident when we compare the frequency of the atomic oscillations with the frequency of the elastic oscillations of a macroscopic crystal. The former is very great in comparison with the latter even for a crystal of colloidal dimensions. Hence the oscillations of the atoms in the interior of a crystal repeat themselves many thousands of times, thereby defining their frequency with all necessary precision, before any disturbance originating in the interior of the crystal could travel out to reach its surface and return after reflection to the place of its origin. Hence, whether the boundary is there or not makes no difference to the modes and frequencies of atomic vibration.

The fallacy of identifying the atomic vibrations with stationary wave-patterns is obvious even in such simple cases as those considered by Debye. The vast majority of the stationary wave-patterns assumed in his theory to be the carriers of the thermal energy of the crystal have wave-lengths of the same order of magnitude as its lattice spacings. These are precisely the circumstances in which it is not permissible to identify the dynamical behaviour of a discrete structure with that of a medium of uniform density. The consequence of such identification is to endow the crystal with an immense number of modes of vibration with frequencies all different from each other throughout the range under consideration and thus to present a false picture of the spectroscopic behaviour of the crystal.

Though Born's theory nominally takes account of the discrete lattice structure of crystals, his "postulate of the cyclic lattice" is equivalent to assuming that the normal modes of vibration of the atoms are similar to the oscillations of the volume elements in a continuous solid having the same shape as the unit cell of the crystal but of greatly enlarged size. The stationary vibrations permitted by the postulate accordingly appear in immense numbers with wave-lengths and frequencies all different from each other



and with their modes wholly unrelated to the structure of the crystal. It is important to remark in this connection that Born does not restrict himself to simple lattice structures but also claims his theory to be valid for all crystals. Any one who appreciates the nature of the results following from Born's lattice theory will realize that the ideology behind his dynamics is completely false. In effect, Born endows the atoms in a crystal with a vast number of modes and frequencies of vibration which are wholly unrelated to its internal architecture and which have a continuous spectrum of frequencies, a result which is in flagrant contradiction with the facts of observation revealed by spectroscopic investigations.

## 6. CONFLICT WITH THERMODYNAMICS

A stationary wave-pattern is a mode of vibration in which all the volume elements of the medium oscillate with the same frequency and in the same or opposite phases and with relative amplitudes which remain invariant with time. Vibrations of this type are characteristic of a macroscopic solid and can be considered as its normal modes of vibration and determined by the methods of the classical theory of elasticity. Such vibrations can also be set up and maintained in an elastic solid artificially, as for example, by the use of a piezo-electric oscillator attached to it.

The identification of the thermal agitation in crystals with stationary wave-patterns of the nature described above which is postulated in the theories of Debye and Born is however clearly irreconcilable with the statistical concept of the nature of thermal energy in material bodies. Thermal agitation is envisaged in Boltzmann's entropy-probability principle as a chaotic and fluctuating disturbance varying in its character and intensity from instant to instant and from place to place within the material. Atomic groups of similar nature which are located in parts of the crystal not contiguous to each other may indeed vibrate with the same frequency. But there can be nothing in the nature of definite relationships either in their amplitudes or in their phases of vibration persisting in time.

The issue can also be put a little differently. A crystal is an assembly of an immense number of individual atoms which are capable of moving from their positions of equilibrium. Hence the state of the system can only be described in terms of the values of a very large number of independent variables. The interactions between neighbouring atoms would naturally influence their relative movements and determine their modes and frequencies of vibration. But we cannot in any circumstances regard the entire assembly as a single unit in the thermodynamic sense or postulate constancy of ampli-



tude or coherence of phase in the atomic vibrations over its entire volume. A description of the thermal agitation in precisely defined terms is possible only for domains of space and periods of time which are small in comparison with macroscopic standards. In other words, the entire ideology behind the theories of Debye and Born is incompatible with the fundamental notions of the nature of thermal energy which lie at the base of the science of thermodynamics.

## 7. MISINTERPRETATION OF THE QUANTUM THEORY

As has been shown above, the theory of specific heats can be placed on a logically sustainable basis only if we recognize that the oscillators which are the carriers of the thermal energy are the structural elements in the crystal. We then obtain a picture of the thermal agitation in the solid which is consistent with the general principles of dynamics and of thermodynamics. Necessarily, therefore, it is these same oscillators whose vibrational energies must be assumed to be quantised. Since, further, these oscillators are present in large numbers distributed over the volume of the crystal, we have a logical justification for the use of Boltzmann's principle in conjunction with the quantum hypothesis for the evaluation of the average energy of the oscillators of any particular frequency and therefrom also the evaluation of the heat capacity of the entire crystal.

To the fallacies which vitiate the Debye and Born theories we have therefore to add one more, *viz.*, that they give a fantastic and altogether meaningless interpretation to the postulates of the quantum theory. They proceed to quantise the energy of the normal modes of vibration of a macroscopic crystal; in doing this, they ignore the fact that the theory of quanta possesses a meaning and significance only in relation to the behaviour of the physical entities which the language of determinism characteristic of macroscopic physics cannot successfully describe. For example, we can speak meaningfully of quantising the energies of rotation or vibration of a molecule of benzene; but it is patently absurd to quantise the vibrations of a tuning fork or the rotations of a flywheel.











